Photocatalytic Properties under Sunlight of Heterostructures AgCl/CuO Obtained by Sonochemical Method

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Received: 14 March 2018 / Accepted: 28 May 2018 / Published online: 13 June 2018 © Springer Science+Business Media, LLC, part of Springer Nature 2018

Abstract

AgCl/CuO heterostructures were synthesized via a sonochemical method. AgCl/CuO molar compositions of 1:1 and 2:1 were prepared, respectively. Such compositions were prepared using three distinct routes. The particles were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM-FEG) and UV-Vis spectroscopy (UV-Vis). In order to analyze the applicability of the heterostructure, photocatalytic tests were performed under sunlight and UV-Vis radiation for the degradation of the methylene blue dye. The results of the X-ray diffraction confirmed the formation of the AgCl/CuO heterostructure in all samples, with no evidence of doping or formation of deleterious phases. SEM images indicate a cubic-like morphology for the AgCl particles, forming Ag⁰ on its surface, the CuO particles have a leaf appearance. The results of the photocatalytic activity indicate that the increase of the AgCl molar ratio from 1:1 to 2:1 accelerates the degradation of methylene blue for both the radiations and shows that sunlight decreases by at least 55% for the degradation of the methylene blue, depending on the composition, to the heterostructure.

Keywords Photocatalysis · Sunlight · Heterostructure · AgCl/CuO · Sonochemical

Introduction

The literature reports that copper and its compounds have been applied as water-sterilizing agents, avoiding the proliferation of microorganisms and associated problems [1–4]. The shape, size, and positive charges on the surface of the particles facilitate the negative bacterial surface binding, resulting in a better bactericidal effect [1, 2]. In the photocatalytic processes using semiconductors, under light radiation, an electron is excited from the valence band to the conduction band, such excitation promotes the generation of a hole in the valence band, where it interacts with H₂O or OH⁻, which are adsorbed on the band (OH), or the electron excited for the conduction band interacts with the O₂ adsorbed, generating O₂⁻ [5].

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Copper oxide has gained a lot of attention in photocatalytic activity because it has a small bandgap (~ 1.2 eV). Silver particles have received great attention in the last decades in the fields of engineering due to their wide field of application, as for example in the catalysis [6], fuel cells [7], and lithium batteries [8]. The effect of silver on antimicrobial activity has also been gaining attention. Ibanesco et al. [9] impregnated silver nanoparticles in ZnO, and with their increase, it also increased antimicrobial capacity against Escherichia coli and Micrococcus luteus bacteria. Metal particles, especially noble metals, generally exhibit high electrocatalytic activities relative to their target compounds. Among these materials, silver and copper particles exhibit catalytic activity for H₂O₂ reduction [10, 11]. Liu et al. [12] produced silver core-shell on copper particles and noticed that silver provides an increase in the photocatalytic activity of the material. Wang et al. [13] deposited Ag⁰ particles on the surface of Cu2O particles and doubled the catalytic efficiency against Pironin B after 150 min.

The synthesis of heterostructures formed by the combination of semiconductors offers an important alternative in the search for the combination of the properties of individual components in a single system [14, 15]. These heterostructured compounds have advantages mainly due to the increase of their capacity as charge separators [16], band bending due to Fermi level



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equilibration [17, 18], surface properties enhancement [19], and increased gas accessibility [20]. Recently, hybrid nanocatalysts with metal particles on their surface, acting to produce a plasmonic effect, have gained great importance in the study of the decomposition of organic pollutants under visible radiation [10, 21, 22]. The plasmonic effect acts by preventing the electron/hole recombination reaction, increasing the photocatalytic efficiency of the material [23]. The literature [24–27] reports that silver nanoparticles deposited on a semiconductor activates the generation of electron/hole pairs and, consequently, increases the photocatalytic activity under the sunlight or the irradiation of visible light.

Conventional methods of synthesis are made in several steps and generally need calcination. In order to eliminate these problems, the method of sonochemical synthesis has been widely used, as it generally does not need several steps or subsequent calcination. In addition, it is considered a "green" synthesis method [23-26]. Besides, ultrasonic radiation accelerates chemical reactions [28-30]. Ultrasonic radiation is basically based on cavitation, where the formation, growth, and collapse of the bubbles formed by the propagation of the waves in the liquid, cause an increase in temperature and very high local pressure [31–33]. Bubble explosions generate high pressure and temperature of the order of nanoseconds, accompanied by sonoluminescence and mechanical effects [33, 34]. Thus, the yield obtained by the sonochemical synthesis method is greater than that obtained by traditional methods, such as sol-gel and pechini [35, 36].

This work investigated the efficiency of the sonochemical synthesis in obtaining the AgCl/CuO heterostructures and obtaining Ag nanoparticles on the surface of the particles without the need for another process. In addition, we also investigated the changes promoted by the synthesis route change and the AgCl/CuO ratio in the photocatalytic properties under UV-Vis radiation and sunlight, photoluminescent properties, and antimicrobial activity against the bacteria *S. aureus* and *E. coli*.

Materials and Methods

Synthesis AgCl/CuO

The AgCl/CuO powders were obtained by a sonochemical method in the Branson 102C tip, operating at a frequency of 20 kHz, through three distinct routes. The heterostructures were obtained in 2 M proportions, AgCl 1:1 CuO (11R1, 11R2, and 11R3), and AgCl 2:1 CuO (21R1, 21R2, and 21R3). For the production of AgCl, AgNO₃ (synth, 99%) and NaCl (Dynamic LTDA, 99%) were used, and for the CuO, Cu(NO₃)₂.2.5H₂O (Alfa Aesar, 98%) and NH₄OH (Synth) were stoichiometrically weighed. These were dissolved in 100 mL of distilled water for the preparation of the solutions, and the PVP was added, in a ratio of 1:1 with the nitrates, for a better morphological control. For comparison purposes, AgCl and CuO particles were synthesized in isolation, maintaining the ratio of 1:1, for 30 min. The three routes of synthesis used are illustrated in Fig. 1. All AgCl/CuO compounds were synthesized at room temperature.

Characterization

AgCl/CuO phase compositions were investigated in a Shimadzu diffractometer (XRD-6000) using CuK α radiation (0.15418 Å). Scanning electron microscopy (SEM) was used to observe the particle morphology. The photocatalytic



properties of the samples were tested (as a catalyst) for the degradation of methylene blue dye (MB) with molecular formula [C16H18ClN3S] (99.5% purity, Mallinckrodt) in aqueous solution under UV-Vis illumination and sunlight. The tests were performed on a quartz cylinder containing 50 mL of methylene blue solution (10-5 mol/L concentration) and 0.05 g of material powder. The UV-Vis light test was performed in a reactor containing six UVC lamps (Philips TVU, 15 W, with maximum intensity of 254 nm = 4.9 eV). The test under sunlight occurred outdoors, between 10:00 and 14:00 h, period of higher solar incidence. UV-Vis spectroscopy was performed on Shimadzu equipment (UV-2600), with a wavelength range of 200 to 800 nm and programmed for the diffuse reflectance mode, where from these results, the band gap energy (Egap) was determined using the Wood and Tauc Equation [37]. The antimicrobial activity of the AgCl/CuO particles were tested against Staphylococcus aureus (grampositive) and Escherichia coli (gram-negative) bacteria by measuring the inhibition halo (disk diffusion method). This test is established as a standard by the NCCLS (National Committee for Clinical Laboratory Standards). A solution containing the AgCl/CuO particles was deposited on a filter disc with 6 mm diameter, which was deposited in the bacterial inoculum (1×108 CFU/mL). The pH of the culture medium remained between 7.2 and 7.4 and the plates were incubated for 24 h at 37 °C in a bacteriological oven. For comparative purposes, the specific antibiotic test (Vancomycin for S. aureus and Gentamicin for E. coli) was performed.

Results and Discussions

The XRD technique was used to determine the purity and crystalline structure of the material synthesized by the sonochemical method. Figure 2a, b shows the XRD diffractograms obtained for the three synthetic routes in the ratios AgCl 1:1 CuO and AgCl 2:1 CuO, respectively.

The diffraction peaks for the AgCl and CuO phases are in agreement with ICSD 64734 and ICSD 92365, having cubic (Fig. 3a) and monoclinic structures (Fig. 3b), respectively. Chen et al. [22] synthesized AgCl nanoparticles by a sonochemical method for 30 min and also obtained the phase referring to the ICSD 64734. The cubic structure, related to AgCl, can be confirmed by the diffraction peaks at 2θ angles of 27.825°, 32.238°, and 46.237° for the planes (111), (200), and (220), respectively.

According to the XRD patterns obtained in Fig. 2a, b, the AgCl/CuO powders exhibit a crystalline and orderly structure at long range. These results show that through the sonochemical method it is possible to obtain the material without several steps or future calcination. There was no formation of secondary phases. Liu et al. [21] synthesized nanoparticles of CuO by hydrothermal method, at 80 °C for 12 h, and obtained a monoclinic phase structure equal to that obtained in this study by means of sonochemical for 30 min.

Using the UnittCell-97 Maud software [36], the Rietveld refinement of the diffractograms obtained from the AgCl/CuO heterostructures was performed through the three different routes. Tables 1 and 2 show the values obtained for the crystallite size, phase in volume percentage, lattice parameters, angle β , and volume of each phase.

The lattice parameter values, and consequently the volume of the unit cells for the AgCl/CuO heterostructure, were very close to the patterns ICSD 64734 and ICSD 92365, respectively. Chen et al. [22] synthesized particles of AgCl, by sonochemical method, with network parameter a = 5.537 Å and volume of 169.75 $Å^3$, close to the one found in this work. Souza et al. [38] obtained CuO particles by the electrical heating of resistors, with lattice parameters a = 4.664 Å, b =3.411 Å, c = 5.115 Å, and $\beta = 99.41^{\circ}$, with a volume of 80.28 Å³, also compatible with those obtained in this work. Table 1 shows that the subsequent synthesis of CuO (route 1) promote the increase of lattice parameter a and reduction of parameters b and c. Route 2 promote the increase of crystallite size of AgCl particles, whereas in CuO this increase is observed when produced by route 3. In addition, route 2

Fig. 2 XRD pattern of the AgCl/ CuO particles obtained by the sonochemical method



100

* AgCl

Fig. 3 Polyhedral representation of structures referring to **a** ICSD 64734 and **b** ICSD 92365



generates a lower percentage of AgCl phase in relation to CuO, contrasting in the worst result of photocatalysis in relation to the other routes.

Figure 4a, c shows the morphology of AgCl and CuO particles obtained by scanning electron microscopy (SEM). Figure 4b, d shows, respectively, the particle size distribution for AgCl and CuO. AgCl presents an irregular aspect and some cubic particles, with a deposition of metallic silver nanoparticles on surface, whereas the CuO particles present a leaflike morphology. Figure 5 shows the distribution of the particles in AgCl/CuO heterostructure. The variation of the proportion of reagents and the route used did not provide morphological changes in the particles. Figure 4e shows EDS spectrum of a silver particle on the surface of the AgCl particle, obtaining the peaks related to $L\alpha 1$ (2.984 keV), $L\beta 1$ (3.151 keV), and L $\beta 2$ (3.348 keV), which are characteristic of silver. Chen et al. [22] also observed the formation of metallic silver on the surface of AgCl particles. Pang et al. [39] mentioned that a uniform and controlled morphology increases the coefficient of light absorption, increasing the number of active sites, improving the photocatalytic properties of materials. Still according to Pang et al. [39], for AgCl/Ag, the cubic morphology is better suited for methyl orange catalysis.

The different types of defects in the structure of the material promote the formation of different intermediate levels between the valence and conduction bands [40]. Thus, these defects promote changes in the electronic structure, affecting the optical properties of the material. Table 3 shows the absorption spectrum in the UV-Vis region of the heterostructures and the isolated materials, respectively. The optical gap was obtained by extrapolating the linear region of the curve according to the Wood and Tauc method [37].

According to Table 3, CuO show less Egap than AgCl. Nemade et al. [41] synthesized CuO nanoparticles by varying the concentration of hexamethylenetetramine, obtaining an Egap = 1.24 eV, very similar to the one found in this work. Table 3 also shows that even with the variation of the route and the proportion of the heterostructures, the Egap remains almost constant, with an average value of 1.44 eV, being slightly higher or pure CuO (1.32 eV) and lower than AgCl (2.8 eV). The lower values of Egap are wished due to the possibility of generating electron/hole pairs with higher wavelength radiation, such as visible light.

Figures 6 and 7 show the variation of the methylene blue concentration by the time under UV-Vis radiation and sunlight for the isolated materials (AgCl and CuO) and, for the heterostructure (AgCl/CuO), respectively. The test was executed in triplicate for a more credible results and the curve of the variation of C/Co versus time shows the mean value. The MB curve was obtained without the presence of a semiconductor. Zhang et al. [42] showed that the addition of silver to the copper substrate doped with titanium dioxide (Cu-TiO2)

Sample		Parameter	Parameter AgCl			
		a (Å)	b (Å)	c (Å)	β (°)	a (Å)
AgCl 1:1 CuO	Route 1	4.6949	3.4310	5.1366	99.3778	5.5509
	Route 2	4.6843	3.4275	5.1408	99.4443	5.5484
	Route 3	4.6840	3.4340	5.1385	99.3229	5.5492
AgCl 2:1 CuO	Route 1	4.6960	3.4286	5.1335	99.4349	5.5500
	Route 2	4.6916	3.4306	5.1409	99.4315	5.5512
	Route 3	4.6840	3.4340	5.1385	99.3229	5.5492
ICSD 64734		-	_	_	_	5.549
ICSD 92365		4.6844	3.4192	5.1231	99.76	_

Table 2Crystallite size,percentage of volume phase, andvolume of the unit cells for theheterostructures obtained by threeroutes

Sample		Dcrys (nm)		Phase in v	Phase in volume (%)		V (Å ³)	
		AgCl	CuO	AgCl	CuO	AgCl	CuO	
AgCl 1:1 CuO	Route 1	168.78	23.71	46.19	53.80	171.03	82.74	
	Route 2	206.68	22.05	34.74	65.25	170.80	82.53	
	Route 3	197.26	34.50	50.88	59.11	170.88	82.65	
AgCl 2:1 CuO	Route 1	210.92	17.47	61.47	38.52	170.95	82.65	
	Route 2	261.90	21.78	51.23	48.76	171.06	82.74	
	Route 3	197.26	34.50	60.88	39.11	170.88	82.65	

increases its photocatalytic activity on the methylene blue dye due to a decrease in the electron/hole recombination rate, resulting in a higher amount of electrons for transition. According to Woo et al. [43], the impediment of electron/ hole recombination provide more electrons free for the transition from the valence band to the conduction band, favoring photocatalysis. In addition, AgCl can generate °Cl which is a strong oxidizing species [44].

The photocatalytic results (Figs. 6 and 7) show that UV-Vis radiation has a higher methylene blue degradation power than visible light, but with the addition of the catalyst, solar radiation acts more efficiently than UV-Vis. According to Teixeira et al. [45], the rate of photocatalytic degradation is independent of light intensity for systems having high illumination. That is, if the catalyst is sufficiently illuminated (absorbed energy greater than Egap), the generation of e^-/h^+ pairs must be independent of the radiation source. Since the energy

supplied in both cases (sunlight and UV-Vis) is higher than Egap of the isolated materials and the heterostructures (shown in Table 3), the generation of the e^{-}/h^{+} pairs occurs efficiently. However, the higher the illumination rate, the more frequent the recombination of e^{-}/h^{+} pairs will be. According to Muruganandham et al. [46], the increase in light intensity results in an increase in the rate of degradation of the organic compounds, in which a linear dependence is observed at low intensities, while at high intensities this behavior is not maintained, and the rate of degradation becomes be a function of the square root of the intensity of light. Ollis et al. [47] emphasized that there are two important concepts in the photocatalytic reactions, quantum yield, and photoefficiency. The former deals with the photons absorbed and used for photoexcitation, and the second deals with the reaction rate observed. The photonic efficiency is higher at low luminous intensities [48]. Figures 4 and 5 also show that Ag^{0} formation







Fig. 5 Images obtained by SEM for the heterostructures AgCl 1:1 CuO **a** route 1, **b** route 2, and **c** route 3 and AgCl 2:1 CuO **d** route 1, **e** route 2, and **f** route 3

occurs only on the surface of the AgCl particles, causing them to act in the production of the plasmonic effect, increasing the photocatalytic activity of the material. Figure 5 shows that routes 1 and 3 present a more homogeneous distribution of the Ag^0 nanoparticles on the surface of the particles, resulting in an optimization of the plasmonic effect, thus increasing the photocatalytic activity [49, 50]. In addition, as shown in Table 2, route 2 presents less amount of AgCl in relation to the others, providing less photocatalytic activity for the heterostructure.

Figure 8a–c shows the photoluminescence curves for the AgCl and CuO compounds and for the heterostructures in the ratios AgCl 1:1 CuO and AgCl 2:1 CuO, respectively. The PL curves presented a broadband in the typical photoluminescent

Table 3 Egap obtained by extrapolation of the Image: state of the	Sample	Egap (eV)	
linear region of the absorption spectrum according to the Tauc method in the UV-Vis region for the AgCl/CuO heterostructures	AgCl 1:1 CuO AgCl 2:1 CuO	Route 1 Route 2 Route 3 Route 1 Route 2 Route 3	1.45 1.44 1.43 1.45 1.45 1.45
	AgCl		2.80
	CuO		1.32

emission spectrum of systems in which the relaxation processes occur in several different ways, involving different intermediate states in the gap of the material [48]. According to this behavior, the PL emission spectra of the investigated heterostructures were decomposed using a Gaussian function with three components. With these decompositions, it may be determined how much each color contributes in the emission. Figure 9 shows the decompositions of the PL curves with the relative percentage of the corresponding color and its maximum peak. Each color in the electromagnetic spectrum represents a set of different electronic transitions and is related to a specific structural arrangement.

Chen et al. [51] observed that silver particles have an absorption band at 450 nm before undergoing UV radiation. Figure 9a shows that the heterostructure produced by route 1 showed displacement in the absorption band to the violet region, a fact that is associated with the later synthesis of CuO related to the AgCl. According to Fig. 9b, c, it can be seen that routes 2 and 3 show some absorption around the blue color, but in route 2, where the synthesis occurs simultaneously, copper acts in a detrimental way to the photoluminescence of the heterostructure, as shown Fig. 8b. Figure 8c illustrates the effect of silver on photoluminescence, where even being synthesized together with copper, its greater amount increases the photoluminescent activity. Botelho et al. [52] obtained Ag₃PO₄ particles with maximum emission at 444 nm in the blue region. The increase in amount of silver is also noticeable





in route 1, where it provides a shift of the band to around blue. Figure 9d–f illustrates the displacement of the bands to greater wavelengths. Increasing the amount of AgCl in route 1 causes the material to lose its contribution in the ultraviolet region and makes it contribute to the green region of the spectrum. The routes 2 and 3 of synthesis show the increase of the influence of the blue component and a reduction of the others. The effects provided by the Cu occur due to its bivalence, where it acts to reduce the number of holes (h⁺) and, therefore, damages the photocatalytic and photoluminescent properties of the heterostructures. Oliveira et al. [53] showed that the addition of copper to the structure of CaTiO₃ (CaCu₃Ti₄O₁₂) significantly decreased the photoluminescence of the material.

The antimicrobial activity was tested against the bacteria *Staphylococcus aureus* (gram-positive) and *Escherichia coli* (gram-negative). The antibiotics Vancomycin (*S. aureus*) and Gentamicin (*E. coli*) were used for control. The diffusion disc technique was used, in which the result is determined by the inhibition halo formed around the sample. Initially, the pure samples were used to determine the best concentration to be used in the heterostructure. The AgCl samples had concentrations of 1, 2, 4, 5, and 10 mg/mL. While the CuO samples varied in 5 and 10 mg/mL. Table 4 shows the inhibition halos formed by these materials.

Table 4 shows that CuO samples did not form an inhibition halo and that the halos formed by the AgCl samples showed



Fig. 7 Variation of the methylene blue degradation as a function of the time for **a** AgCl 1:1 CuO, **b** AgCl 2:1 CuO under UV-Vis radiation, and **c** AgCl 1:1 CuO, **d** AgCl 2:1 CuO under sunlight



Fig. 8 Photoluminescence for compounds a AgCl and CuO and heterostructures obtained in proportions, b AgCl 1:1 CuO, and c AgCl 2:1 CuO

no significant difference. With the results of Table 4, the concentration of 5 mg/mL for the AgCl/CuO heterostructure was established. Figure 10 shows the inhibition halos formed by these heterostructures against *S. aureus* and *E. coli* bacteria.

The AgCl/CuO heterostructures presented antimicrobial activity superior to the isolated AgCl and CuO compounds, showing that there are positive effects of the interaction between the compounds. Neto et al. [54] showed through an experimental design that increasing the amount of PVP promotes a reduction in the size of the AgCl particles. In addition, it provides an increase in the photocatalytic properties against the methylene blue dye. However, because it is a polymer, it can act negatively in the antimicrobial activity [55, 56].

Sheehy et al. [57] synthesized silver nanoparticles stabilized with PVP and performed a study varying their concentration from 10 to 100 ppm and, for all concentrations, it did not obtained the formation of inhibition halos against *E. coli* bacteria. The particle size is an important factor on antimicrobial activity, in which the larger its surface area, the better the results obtained [53]. The AgCl/CuO particles had no nanometric structure, and it may be the cause of their low activity. Jurek et al. [55] observed that the increase in Ag-Pt/TiO2 particle size negatively influences the antimicrobial properties against *E. coli* and *S. aureus* bacteria. Bera et al. [56] studied the antimicrobial activity of silver nanoparticles, varying their size, and reported that their increase impairs such



Fig. 9 Deconvolution of the PL emission curves of the heterostructures obtained in the proportions AgCl 1:1 CuO by the **a** route 1, **b** route 2, and **c** route 3 and AgCl 2:1 CuO by the **d** route 1, and **e** route 2 and **f** route 3.

UV = ultraviolet component, VIO = violet component, AZU = blue component, CIA = cyano component, VER = green component

Table 4Inhibition halo diameter(mm) for AgCl and CuO varyingthe concentration

Sample		Inhibition halo diameter (mm) for <i>Staphylococcus aureus</i>	Inhibition halo diameter (mm) for <i>Escherichia coli</i>
AgCl	1 mg/mL	9.22 ± 0.016	9.45 ± 0.091
	2 mg/mL	9.34 ± 0.070	9.18 ± 0.307
	4 mg/mL	9.93 ± 0.026	9.82 ± 0.145
	5 mg/mL	9.58 ± 0.092	9.76 ± 0.0351
	10 mg/mL	10.11 ± 0.138	9.87 ± 0.183
CuO	5 mg/mL	6	6
	10 mg/mL	6	6
Vancomyci	in	18.33 ± 0.023	_
Gentamicir	1	_	18.30 ± 0.017

activity against *S. epidermidis*, *B. megaterium*, *E. coli*, and *P. aeruginosa* bacteria.

Conclusion

The sonochemical method was shown to be simple and efficient to obtain the heterostructures, not requiring a subsequent calcination. The variation in the ratio and in the synthesis routes did not change the phases of the heterostructure (AgCl/CuO). It was noticed that the alteration of the synthesis route provided different photocatalytic behaviors, where routes 1 and 3 presented similar results and route 2 presented the worst performance when irradiated by sunlight and UV-Vis. The AgCl/CuO heterostructure showed superior photocatalytic activity when irradiated with sunlight, related to UV-Vis, presenting a reduction of at least 55% in the degradation of methylene blue. The increase in the ratio of AgCl provided an acceleration in the reduction of the methylene blue



Fig. 10 Antimicrobial activity of AgCl/CuO heterostructure against *S. aureus* (a) and *E. coli* (b) bacteria

concentration. The particles of AgCl presented metallic silver deposited on their surface, where these particles act producing a plasmonic effect, positively influencing the photocatalytic activity of the material. Simultaneous synthesis and addition of CuO following the silver causes a reduction in the photoluminescent properties, a fact that loses relevance when the ratio AgCl/CuO is changed from 1:1 to 2:1. SEM images show the cubic morphology of AgCl particles, whereas CuO particles show a leaf-like morphology. CuO showed no antimicrobial activity against the *E. coli* and *S. aureus* bacteria, whereas the AgCl showed a low activity compared to the reference. The AgCl/CuO heterostructure showed higher antimicrobial activity than the AgCl, showing interaction among the compounds.

Acknowledgements The authors thank the financial support of the Brazilian research financing institutions: CAPES, CNPq No. 402127/2013-7, and FAPESP 2013/07296-2.

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