

Preparation of Au_n quantum clusters with catalytic activity in β-cyclodextrin polyurethane nanosponges

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ABSTRACT

Here we report the use of β-cyclodextrin polyurethane nanosponges cross-linked with 1,6-hexamethylene diisocyanate as a template for the preparation of Au_n quantum clusters, by the core-etching of glutathione-capped Au nanoparticles. The study of temporal evolution of the core-etching process using different Au concentrations indicated that formation of Au_n clusters embedded in the nanosponge is favored by the use of lower Au concentrations, since it began at shorter times and lead to higher cluster loading. An estimation of the number of Au atoms based on the maximum photoluminescence wavelength suggested that, depending on the Au concentration and the core etching time, clusters with 11–15 atoms were formed. After excluding the possibility of an inclusion complex formation, evaluation of the catalytic activity of nanosponge-loaded Au_n clusters toward the reduction of 4-nitrophenol has shown that the reaction is catalyzed by the Au_n clusters with no induction time, following the Langmuir–Hinshelwood kinetic model.

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1. Introduction

Metal clusters with sizes ranging from subnanometric to 1–2 nm, including mainly Au, Ag, Cu, Pd and Pt, are very interesting materials which attract both fundamental and technological interest (Lu & Chen, 2012). Many works are dedicated to understand why representatives with specific numbers of atoms (so called magic numbers) exhibit increased stability than others as well as to model their electronic structures while other works aim to develop synthetic strategies and applications (Maity, Xie, Yamauchi, & Tsukuda, 2012). It has been recognized that clusters with some specific numbers of atoms are particularly more stable than others due to both geometric and electronic factors (Walter et al., 2008; Weigend & Ahlrichs, 2010). Although no explanation alone can account for the stability of all clusters considered magic, some authors have

verified that magic clusters present closed geometric shells while others exhibited closed electronic shells (Díez & Ras, 2011). Metallic clusters in general exhibit size-dependent luminescence properties in the visible range as a result of quantum confinement and molecular-like energy levels, opening the possibility of applications as sensors and markers in imaging and labeling (Díez & Ras, 2011). In this context Au clusters are the most studied among the possible metals due to their higher chemical stability, biocompatibility and well established preparation methods (Zheng, Zhou, Yu, & Liu, 2012).

Regarding the preparation strategies, like other nanomaterials, metal clusters are obtained both by bottom-up and top-down methods (Lu & Chen, 2012). The former includes reduction of metal cations and atom-by-atom growth of the cluster while the latter involves preparation of larger precursor particles from which surface atoms are removed by ligand-induced etching. It was found that this etching process by excess ligands is due to the strong interaction between metal atoms and protecting ligands (Negishi, Nobusada, & Tsukuda, 2005), with the formation of Au(I)SR polymer compounds which can be found as insoluble material after precipitation of the etched product (Schaaff & Whetten, 1999).

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Whatever the method is used, protection of cluster surface against coalescence is necessary since clusters are thermodynamically unstable and undergo spontaneous coalescence in order to reduce the total surface area (Daniel & Astruc, 2004). This can be avoided by use of ligand molecules with high chemical affinity for surface atoms forming a protective layer, among other alternatives such as immobilization onto solid supports. In this context, Negishi et al. (2005) reported the first size-selective synthesis of Au:SR clusters with well-defined chemical formulae by reducing Au^{3+} ions in the presence of glutathione (GSH) followed by separation with poly(acrylamide) gel electrophoresis. They observed that $\text{Au}_{25}\text{SG}_{18}$ cluster is the most thermodynamically stable among all sizes detected. In another important work, Shibu and Pradeep (2011) demonstrated that core-etching of precursor 2–3 nm GSH-protected nanoparticles with excess GSH in cyclodextrin (CD) aqueous solutions lead to the stabilization of Au_{15} clusters trapped in the cavities. The same research group used this same material and prepared luminescent, freestanding composite films for metal ion sensing by soaking chitosan films in Au_{15} cluster solution (George, Shibu, Maliyekkad, Bootharaju, & Pradeep, 2012).

With regard to the catalytic properties, in general gold is described as catalytically inert as a result of its filled d bands which leads to higher activation barriers than other transition metals (Li & Jin, 2013; Lu & Chen, 2012). However, gold clusters exhibited enhanced catalytic activity in many important reactions such as low temperature oxidation of CO to CO_2 , aerobic oxidation of alcohol, selective oxidation of styrene to an aldehyde and epoxide, and partial oxidation of propene to epoxide (Tsunoyama, Ichikuni, Sakurai, & Tsukuda, 2009; Zhu, Qian, & Jin, 2011; Zhu, Qian, Zhu, & Jin, 2010). It has been shown that gold nanoparticles (AuNPs) can activate sp^3 , sp^2 , and sp^1 C–X bonds (X = C, H, halogen, boronic acid, etc.), as well as O_2 , H_2 , among others, giving access to new reaction pathways (Corma, Juez, et al., 2011; Corma, Leyva-Perez, & Sabater, 2011). Meseguer, Cabrero-Antonino, Dominguez, Leyva-Perez, and Corma (2012). This same group reported that Au(I) and Au(III) salts or gold complexes form 3- to 10-atom gold clusters in solution at room temperature and can act as extremely active catalysts, achieving a catalytic activity nearly five orders of magnitude higher than those previously reported (Meseguer et al., 2012). Finally among the many reactions that are catalyzed by AuNPs and clusters, the reduction of 4-nitrophenol (4NP) and other nitroaromatics stands as a major challenge because of the pollutant nature of these compounds (Zhao, Feng, Huang, Yang, & Astruc, 2015), which are anthropogenic, toxic and growth inhibitor of microorganisms in nature, which is undesirable for biodegradation. Moreover, this can be considered as model reaction since it proceeds from a single reactant to a single product (4-aminophenol) and its progress is negligible in the absence of a catalyst. Several works have evaluated the performance of different nanoparticle systems in catalysis (Kumar, 2014; Yamamoto et al., 2012; Zhou, Xu, Liu, Panda, & Chen, 2010), and a large number of them uses the reduction of 4-nitrophenol with promising results (Kumar, 2014; Yamamoto et al., 2012). Yamamoto compared the activities of dimethylformamide-stabilized gold clusters with the GSH (SG) stabilized gold clusters, $\text{Au}_{25}(\text{SG})_{18}$, observing that the latter had a 3 times higher activity than the former. Also, an induction time was observed in the case the dimethylformamide-stabilized gold clusters for the catalytic process to start which was assigned to diffusion-controlled adsorption of reactants onto the surface of the metal catalyst (Yamamoto et al., 2012). This means that in the case of $\text{Au}_{25}(\text{SG})_{18}$ the active sites were not hindered electronically or sterically.

Herein, we describe the preparation of a polyurethane nanosponge based on the reaction of β -cyclodextrin (β -CD) and hexamethylene diisocyanate (HDI), as well as, the synthesis of glutathione-stabilized Au clusters in the β -CD cavities of this polymer, an approach analogous to that described by Shibu and Pradeep

Table 1

Concentrations and volumes of reactants used in the preparation of precursor Au nanoparticles and in the core-etching step.

Precursor Au nanoparticles			Core-etching
$[\text{Au}^{3+}]$ (mol L^{-1})	[GSH] (mol L^{-1})	V 0.2 mol L^{-1} NaBH_4 (mL)	Mol amount GSH (mmol)
0.005	0.01	3.12	0.5
0.01	0.02	6.24	1.0
0.02	0.04	12.5	2.0

(2011). Our aim was at evaluating if the β -CD cavities covalently bound to a solid material would still be able to act as template to the stabilization of Au clusters different from the $\text{Au}_{25}\text{SG}_{18}$ (expected to be favored in aqueous suspension). Another aim was at obtaining Au clusters directly in the solid phase, which are suitable for applications. The nanosponge with embedded Au clusters was then evaluated for its catalytic activity toward 4-nitrophenol reduction from aqueous solutions.

2. Materials and methods

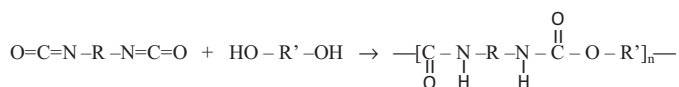
2.1. Materials

β -Cyclodextrin (β -CD), hexamethylene diisocyanate (HDI) and reduced glutathione (GSH) were purchased from Sigma–Aldrich (St. Louis, MO, USA). N,N-dimethyl formamide (DMF), methanol were purchased from Synth (Diadema, SP, Brazil) and $\text{AuCl}_3 \cdot 3\text{H}_2\text{O}$ were purchased from Synth and NaBH_4 from Vetec (São Paulo, SP, Brazil).

The cyclodextrin-based polyurethane polymer (CD-nanosponge) was prepared according to methodologies described in the literature (Araújo et al., 2012; Ozmen & Yilmaz, 2007). β -CD was previously dried in a vacuum oven at 80°C for 24 h. 40 mL of a DMF solution containing 2 g (1.69 mmol) of β -CD was mixed with 2.07 g of HDI (11.8 mmol) and 0.09 mmol tin octanoate. The mixture was heated in a CEM MARS 5 microwave digestion system at 80°C for 30 min. After cooling to room temperature, the polymer was precipitated by the addition of ethyl alcohol, filtered and washed with water and acetone and dried in a vacuum oven at 80°C for 24 h. Nanosponge powder was dispersed in KBr (1 wt%) and pressed into pellets that were characterized by Fourier transform infrared spectroscopy (FTIR), in a Perkin Elmer Spectrum BX. X-ray diffractometry (XRD) were performed with a Rigaku Mini Flex II with 2°min^{-1} scan rate in the $5\text{--}55^\circ$ scan range in 2θ operating with a $\text{Cu K}\alpha$ ($\lambda = 1.5418 \text{ \AA}$), 40 mA current and 30 kV voltage. Thermal analyses (thermogravimetry, TG) were performed with a TA 2960 with N_2 atmosphere, using a heating rate of $10^\circ\text{C min}^{-1}$ in an alumina pan.

2.2. Preparation and characterization of Au clusters

The procedure based on the work by Shibu and Pradeep (2011) started with preparation of the precursor gold nanoparticles by the reduction of Au^{3+} by NaBH_4 in the presence of GSH. For the evaluation of the effect of the initial Au^{3+} concentration, methanol solutions of $\text{AuCl}_3 \cdot 3\text{H}_2\text{O}$ were prepared and cooled to 0°C (see Table 1 for the amounts of reagents used). An appropriate amount of GSH was dissolved in 25 mL of each Au^{3+} solution and the mixtures were kept under stirring for 30 min at 0°C , followed by the fast addition of an aliquot of 0.2 mol L^{-1} NaBH_4 and stirring at 0°C for 1 h. Then, the solid product was collected by centrifugation and washed with methanol. Nanoparticles were characterized by UV/Vis spectroscopy in a Perkin Elmer Lambda 45 Spectrophotometer and transmission electron microscopy (TEM) in a Jeol JEM 1400Plus operating at 120 kV. For TEM images samples were deposited after



Scheme 1. General reaction involved in the preparation of polyurethanes.

sonication in isopropyl alcohol in copper grids coated with an ultra-thin carbon film (Ted Pella, Inc.). Solvent was evaporated at 50 °C.

For nanocluster preparation, just after centrifugation the whole amount of gold nanoparticles precipitated in each experiment was redispersed in distilled water followed by the addition of predetermined GSH masses (see Table 1) and 0.125 g of the CD-nanosponge. The mixtures were heated under reflux at 70 °C for 3, 24, 28 and 72 h. Individual experiments were carried out for each reaction time and, at the end of reaction, the solids were centrifuged, washed with ethanol and dried at ambient conditions. Samples were characterized by UV/Vis reflectance spectroscopy using an Ocean Optics HR2000 spectrophotometer coupled to an integrating sphere. Photoluminescence (PL) measurements were carried out using a Horiba Jobin Yvon model Fluorolog – 3 (Horiba FL3 – 22iHR320) with double monochromators for excitation and emission, using a 450 W Xe lamp source. Transmission electron microscopy (TEM) images were acquired with a Jeol JEM 1400Plus operating at 120 kV.

2.3. Catalysis of 4-nitrophenol (4NP) reduction

A 15 µL of a 10 mmol L^{−1} aqueous solution of 4-nitrophenol (4NP) was placed in a test tube along with 3 mL of a 10 mmol L^{−1} aqueous solution of NaBH₄. An amount of 0.00177 g of the nanosponge embedded Au clusters (sample obtained from 0.005 mol L^{−1} Au³⁺ and etched for 72 h) was added and the absorption spectra measured at different times to monitor the reduction process, using a Perkin Elmer Lambda 45 Spectrophotometer. An analogous procedure using the parent (cluster-free) nanosponge was also carried out for an equivalent time interval to evaluate the possibility of absorbance decrease of 4NP by adsorption or host–guest inclusion process into the CD cavities present in the polymer.

3. Results and discussion

3.1. Preparation of β-cyclodextrin polyurethane nanosponges

The first step was the synthesis of the β-CD polyurethane nanosponge. Polyurethanes are versatile polymers that can be obtained by the reaction between a diisocyanate (O=C=N–R–N=C=O) and a polyol (HO–R'–OH) with characteristic formation of the urethanic carbonyl group (Król, 2007) as can be represented by the reaction (Scheme 1).

Thus the most direct evidence of the formation of a polyurethane polymer comes from the presence of the urethanic carbonyl stretching in the FTIR spectrum, Fig. 1. Here we used hexamethylene diisocyanate and β-CD as the polyol. FTIR spectrum of native β-CD is characterized by bands at 3341 cm^{−1} (OH stretching), 2927 cm^{−1} (CH stretching), 1419 cm^{−1} and 1333 cm^{−1} (in-plane angular bending from primary and secondary alcohols, respectively) and at 1157 cm^{−1} (C–O–C stretching from pyranose rings). After reaction with HDI, the spectrum of the product shows that not every hydroxyl groups have reacted – as expected considering the high number of OH groups in β-CD – as indicated by the presence of the band at 3356 cm^{−1}. The most important feature is the observation of a band at 1712 cm^{−1}, assigned to the urethanic carbonyl stretching along with absence of vibrations near 2270 cm^{−1}

characteristic of free isocyanate (Ylgör, Ylgör, Gulen, Ward, & Wilkes, 2006) evidences the formation of the nanosponge.

Since solid β-CD exhibits some degree of crystallinity, as revealed by the presence of diffraction peaks in its XRD pattern (Fig. 1c), the nanosponge was also characterized to evaluate the effect of polymerization on the crystalline ordering. The diffraction pattern of the solid nanosponge (Fig. 1d) is characterized by the presence of amorphous halos suggestive of a non-crystalline character. This is common behavior for polyurethanes, particularly because of the polyol that imply several OH groups, which participate in the reaction (Araújo et al., 2012). This contributes to random cross-linking and precludes a regular stacking of polymer chains, which would be necessary to the formation of a crystalline polymer.

The thermal behavior of the nanosponge was also compared to that of β-CD, Fig. 2a and b, which shows thermogravimetric (TG), and derivative thermogravimetric (DTG) curves. Comparing the TG and DTG curves of β-CD with that of the nanosponge, the first mass loss up to 100 °C assigned to release of water molecules indicates that β-CD contains a higher amount of humidity, as consistent with the higher number of OH groups. The following mass loss starts at similar temperatures for both samples (250 °C for the nanosponge and 270 °C for β-CD with peaks at 330 °C and 315 °C respectively), being assigned to cleavage of urethanic bonds (nanosponge) and thermal decomposition of β-CD units (Araújo et al., 2012; Petrovic, Zavargo, Flynn, & Macknight, 1994).

3.2. Preparation of Au nanoclusters

As initial step, we prepared glutathione-stabilized Au nanoparticles to be used as precursor for Au clusters by core-etching. TEM image of the as-prepared nanoparticles shows predominant nearly spherical shapes with diameter distribution from 1.5 nm to 8.5 nm and average diameter of about 4.5 nm (data not shown). The nanoparticles were used in the further steps to obtain Au clusters by core-etching using GSH.

In nanocluster formation, the effect of the Au:nanosponge ratio on the nanocluster formation step was studied varying the initial Au³⁺ concentration along with reaction time. This study was monitored by UV/Vis and PL spectroscopies, measured in the solid state for samples isolated from reaction medium. In order to discuss the results, we must recall that Au clusters are subject to quantum confinement effects with consequent increase in the HOMO–LUMO energy gap with size decrease. Thus, band shifts to shorter wavelengths must be interpreted as an increment of clusters with lower numbers of Au atoms. Observing spectra in Fig. 3, it is clear that in general the increase in reaction time lead to the formation of smaller clusters and that this happened faster for the lower Au³⁺ concentration (48 h for 0.005 mol L^{−1} versus 72 h for 0.01 mol L^{−1}). Also, bandwidth decreased with reaction progress suggesting a size focusing. Regarding the possibility of size estimation, a systematic study relating both the position of the maximum of absorption band and the absorption threshold with cluster size is described by Negishi et al. (2005). Based on Negishi et al. (2005) analysis, the bands observed here at 490–510 nm (with thresholds above 700 nm) can be tentatively assigned to clusters with 18–25 atoms while the significantly sharper band with maxima near to 405 nm (threshold at 470 nm) can be due to smaller clusters possibly with 15 Au atoms or less. Actually, this was observed after cluster fractionation and analyses by mass spectrometry, which is a method commonly used to evaluate composition of clusters protected by low molecular weight ligands, such as GSH.

PL spectra added important information on the progress of Au cluster formation (Fig. 4). First, the observation of photoluminescence provides a strong evidence of the presence of Au clusters. As PL results allowed a more detailed discussion, we also studied a higher Au³⁺ initial concentration and two different excitation

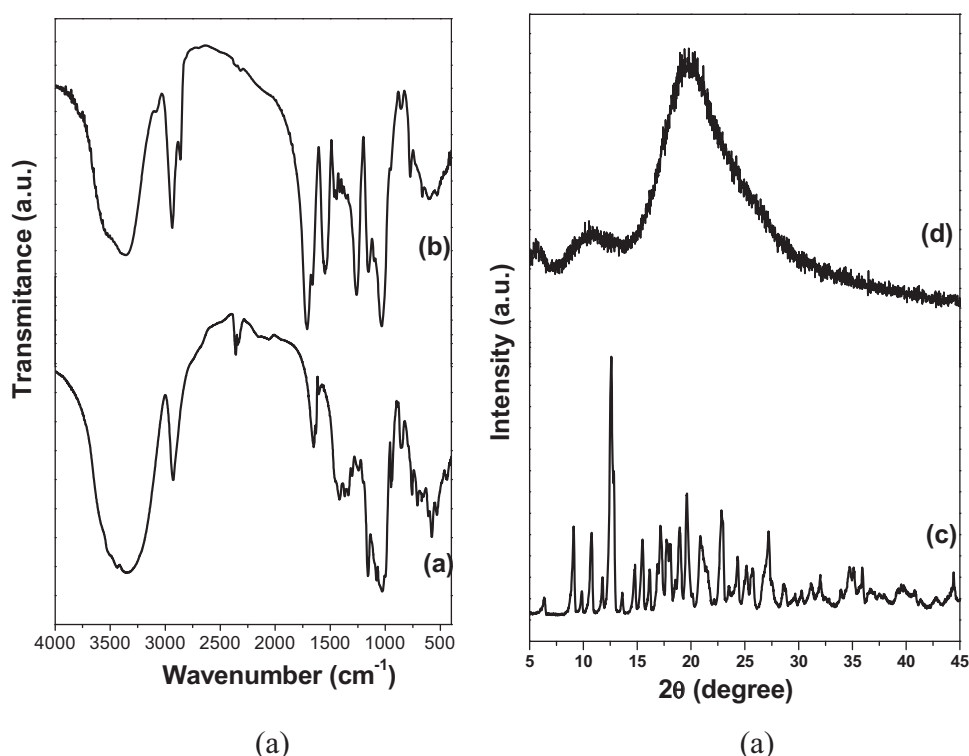


Fig. 1. FTIR (left) and XRD pattern (right) of original β -CD (a, c) and the resulting nanosponge (b, d).

wavelengths (369 nm and 277 nm), considering the possibility of selectively excitation of different-sized clusters within the whole samples. Based on quantum confinement considerations, the use of lower excitation energy will excite selectively only the larger clusters, while both larger and smaller clusters will be excited with higher excitation energy (also adding information about the relative emission intensities from clusters of different sizes).

Before discussing the effects of time, concentration and excitation wavelength, we shall note that main differences in the

whole series of spectra referred to changes relative intensities of emissions at three specific regions: (i) below 500 nm (417 nm and 440 nm) which can be due to clusters with less than 10 Au atoms, as previous reports that $\text{Au}_7(\text{SG})_2$ clusters emit at 426 nm (Ray et al., 2015); (ii) bands around 612–614 nm and 630–640 nm due to clusters 11–15 atoms and (iii) emissions above 700 nm possibly due to clusters with 25 atoms or more, which in the present case can be present outside β -CD cavities. We base these considerations on some previous works. The most stable glutathione-stabilized Au

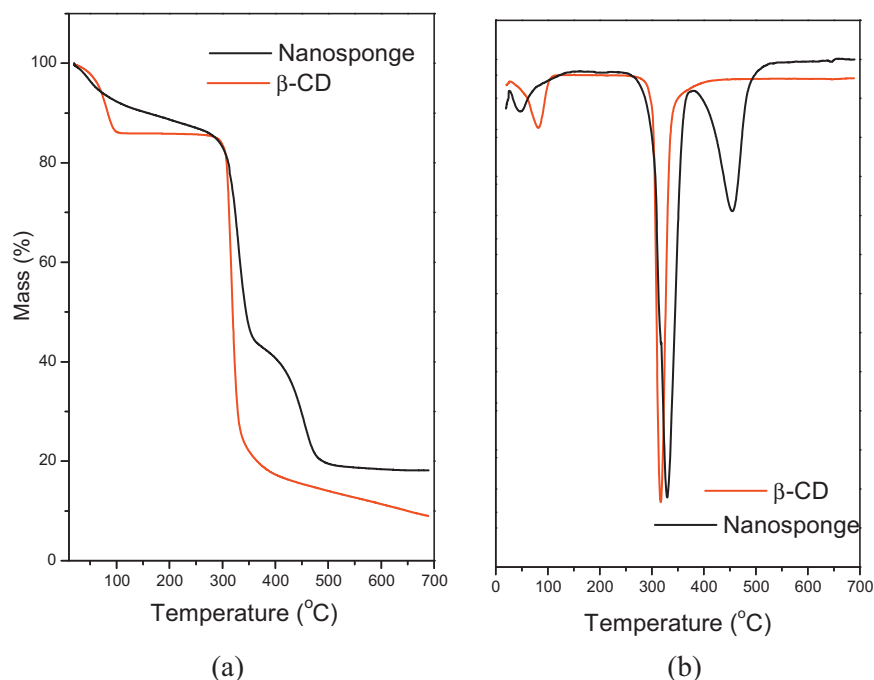


Fig. 2. (a) Thermogravimetric (TG), (b) derivative thermogravimetric (DTG) curves for original β -CD and the resulting nanosponge.

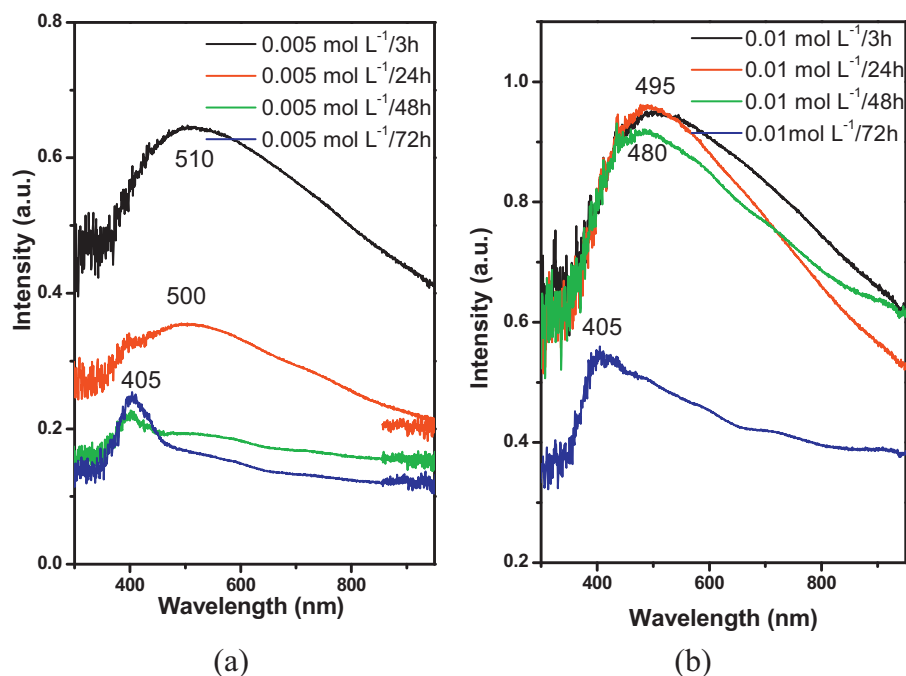


Fig. 3. UV/vis reflectance spectra of solid nanosponge-embedded Au_n clusters, for the study of temporal evolution of the core-etching for different initial HAuCl_4 concentrations: 0.005 mol L^{-1} (a) and 0.01 mol L^{-1} (b).

cluster is $\text{Au}_{25}(\text{SG})_{18}$ (Negishi et al., 2005) while Au_{15} is favored by inclusion into the cavities when the core-etching is carried out in a β -CD solution (Shibu & Pradeep, 2011). A study of the dependence of emission position with cluster size has shown that the characteristic emissions were systematically shifted following changes in cluster size: Au_{22} (679 nm), Au_{23} (685 nm), Au_{25} (700 nm) and Au_{33} (750 nm) (Muhammed et al., 2009). After this systematic study Wang, Wu, Chi, and Chen (2014) proposed an empirical linear relationship ($\lambda_{\text{em}} = 6.4548n + 537.29$, where λ_{em} is the maximum emission wavelength and n is the number of Au atoms) to estimation of the number of Au atoms in this family of clusters, proposing that core etching of $\text{Au}_{25}(\text{SG})_{18}$ cluster in β -CD leads to $\text{Au}_{13}(\text{SG})_8$ cluster.

Using the same expression to estimate the number of Au atoms in our samples, we estimate that the emissions at 612–614 nm are due to clusters with 11–12 atoms while those at 639 nm and 710 nm are due respectively to clusters with 15 and 26–27 atoms.

Upon excitation at 369 nm, after 3 h and 24 h (Fig. 4a and b) the 0.005 mol L^{-1} sample exhibited the emission at 639 nm with higher intensity than the other concentrations, indicating that 0.005 mol L^{-1} sample already contained Au_{15} clusters. The other samples apparently did not contain a significant cluster amount yet to give signal. After 48 and 72 h (Fig. 4c and d), emissions above 700 nm were observed for most of the samples (except the 0.005 mol L^{-1} after 48 h), indicating that clusters with more than 25 atoms were present. This does not exclude the presence of smaller clusters since their emissions were actually masked, as can be seen with excitation at 277 nm which were dominated by emission from smaller clusters (remembering that the same samples were excited with both wavelengths). The whole picture comes from excitation with 277 nm (Fig. 4e–h), capable of exciting a more complete population within the samples. After 3 h and 24 h (Fig. 4e and f), spectra were not very different from those with excitation at 369 nm, except from the higher intensity after 3 h and shift to 614 nm for the 0.005 mol L^{-1} sample. This indicates that there is a higher amount of smaller clusters than detected before. The differences between the two excitation wavelengths are more pronounced after 48 h and 72 h (Fig. 4g and h): only the sample 0.01 mol L^{-1} exhibited larger

clusters while for other samples, Au_{11} and Au_{15} clusters predominated. Observing the whole series of spectra, including absorption spectra, we chose sample $0.005 \text{ mol L}^{-1}/72 \text{ h}$ of etching for application study, although from PL sole data, the $0.005 \text{ mol L}^{-1}/48 \text{ h}$ seems better due to the complete absence of larger clusters. Actually we consider that both samples are probably very similar.

The general effect of the initial Au^{3+} concentration can be understood in terms of the relative proportion with the nanosponge, remembering that the GSH: Au proportion was kept constant during every step of the process. Our results show that a larger proportion of the nanosponge toward gold nanoparticles (corresponding to the 0.005 mol L^{-1} sample) in the core-etching allows faster loading of $\text{Au}_{11}/\text{Au}_{15}$ clusters as well as a higher cluster loading in the nanosponge. It should be emphasized that we characterized only what reached the solid phase, since probably a large part of the core etching occurred in the liquid phase. If this is true, the solid-phase assisted process is favored by the lowest Au concentration. Otherwise, gold nanoparticle core-etching process is more efficient for the 0.005 mol L^{-1} sample. Generalizing the observations for the 0.005 mol L^{-1} sample, at shorter times the cluster formation in nanosponge begins in the β -CD cavities with Au_7 and Au_{15} clusters. As the reaction proceeds the cluster concentration in cavities increases as the emission intensities of $\text{Au}_{11}/\text{Au}_{15}$ clusters increases. Larger clusters, which cannot be accommodated in the cavities but may interact with other functional groups such as carbonyls and nitrogenated groups can also be detected after 72 h, probably in low concentration since their emission is not detected with excitation of 277 nm. Finally for the 0.01 mol L^{-1} and 0.02 mol L^{-1} concentrations the emissions were weak for all reaction times, probably because of an inefficient core-etching or the cluster formation occurred predominantly in the liquid phase so few clusters reached the solid phase. Scheme 2 resumes the temporal evolution of the material for the 0.005 mol L^{-1} concentration.

Excitation spectra, Fig. 5, were also measured. In general excitation spectra showed a single or two excitation bands with no significant change in positions, depending on the sample: excitation maxima were observed close to 275 nm and 350 nm. Is it worth to mention that Shibu and Pradeep (2011) reported

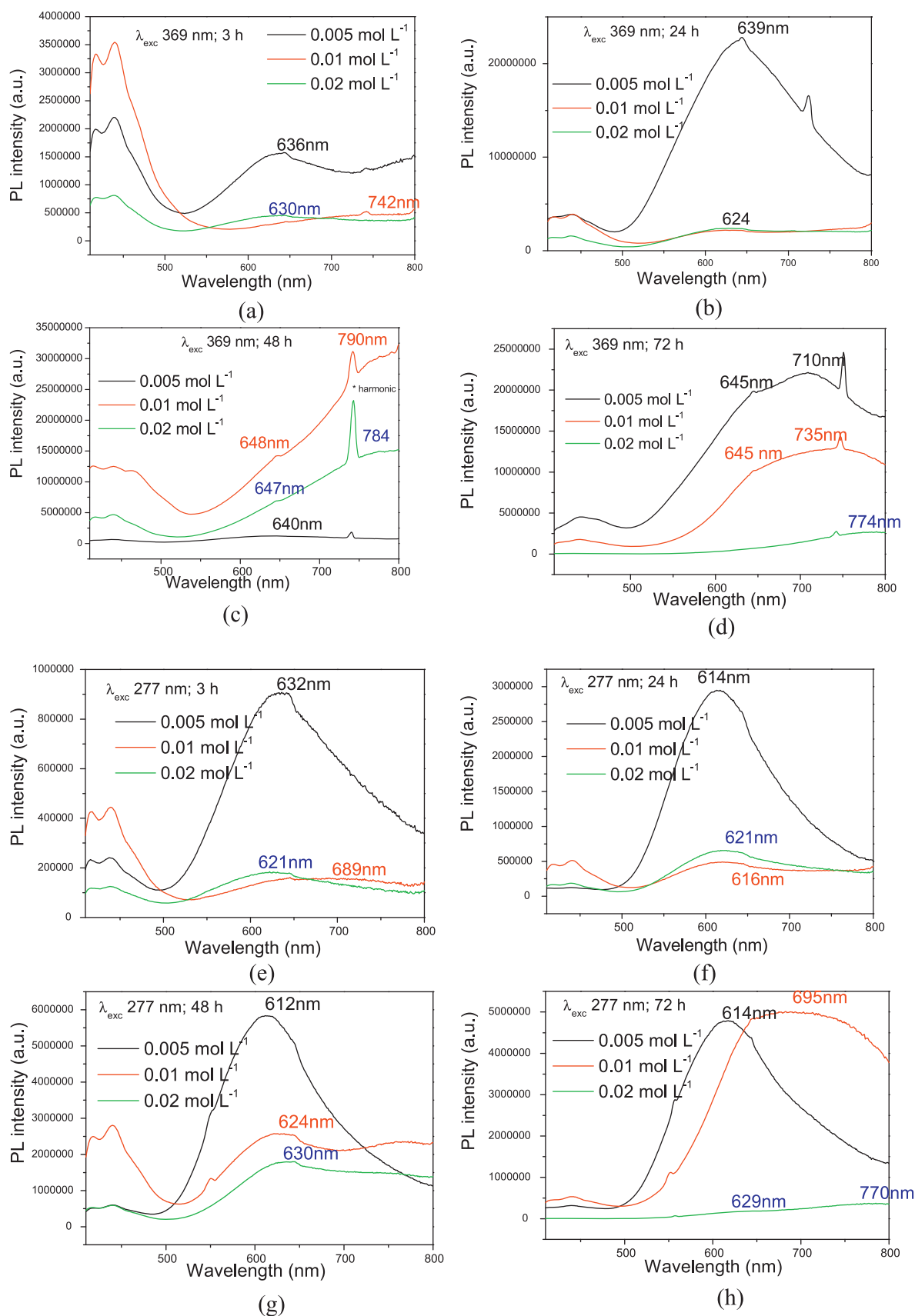
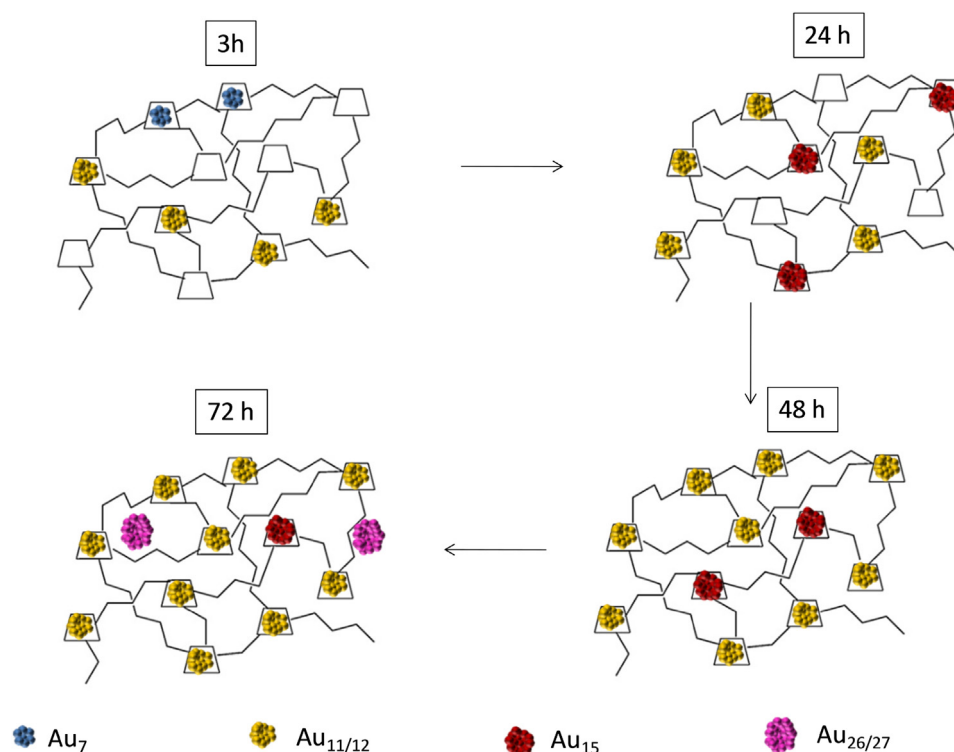


Fig. 4. Photoluminescence spectra of solid nanosponge-embedded Au_n clusters, for the study of temporal evolution of the core-etching for different initial HAuCl_4 concentrations and different excitation wavelength: (a–d) 369 nm; (e–h) 277 nm.



Scheme 2. Idealized representation of the temporal evolution of the material structure for the 0.005 mol L⁻¹ concentration.

excitation maximum at 375 nm for Au₁₅ clusters. Here the excitation spectra suggest that the main contribution to the emissions may come from Au₁₅ clusters and smaller clusters – probably Au₁₃ or Au₁₁. The spectra confirm that the 0.005 mol L⁻¹ concentration favored core-etching in the solid phase – due to higher intensities, which decreased progressively with increasing concentration, and suggest that after 48 h the smaller clusters are predominant.

Although it has been discussed that the observation of ultrasmall metal clusters by electron microscopy techniques is made difficult due to both the reduced size and to the possibility of melting effects of tiny nanoclusters under electron beam heating during the imaging (Lu & Chen, 2012), we acquired some images at 120 kV, only as an attempt to observe the contrast distribution along the material, Fig. 6. Some darker regions can be observed suggesting the presence of Au clusters, which predominate in determined regions. Also groups of dark points with subnanometric size can be observed, marker with circles in the image, whose exact size cannot be measured with accuracy due to the inherent uncertainty of TEM images. Nevertheless we cannot assign these points unequivocally to the clusters.

3.3. Catalysis of 4NP reduction by the nanosponge-encapsulated Au clusters

The reduction of 4NP by NaBH₄ was chosen as a model reaction to evaluate the catalytic activity of nanosponge-encapsulated Au clusters. The reaction progress was monitored by UV–Vis spectroscopy as the intensity of the characteristic band of 4NP at 400 nm progressively decreases while that of 4-aminophenol (4AP) increases. As the parent cyclodextrin nanosponge is also reported as capable of inclusion of molecules from solution (Mohamed, Wilson, & Headley, 2015), with potential application in environmental remediation (Li & Ma, 2000), chromatographic separations and also drug carrier (Tejashri, Amrita, & Darshana, 2013), it was necessary to exclude the possible absorbance reduction by inclusion of 4NP into the β-CD cavities. Thus an analogous experiment was carried out with the nanosponge without the clusters, Fig. 7a. Clearly at time scale in which the reduction takes place, the absorbance of 4NP solution remained constant, since probably this process has a longer characteristic time scale. On the other hand, in the presence of Au clusters, Fig. 7b, the reaction reaches completion after

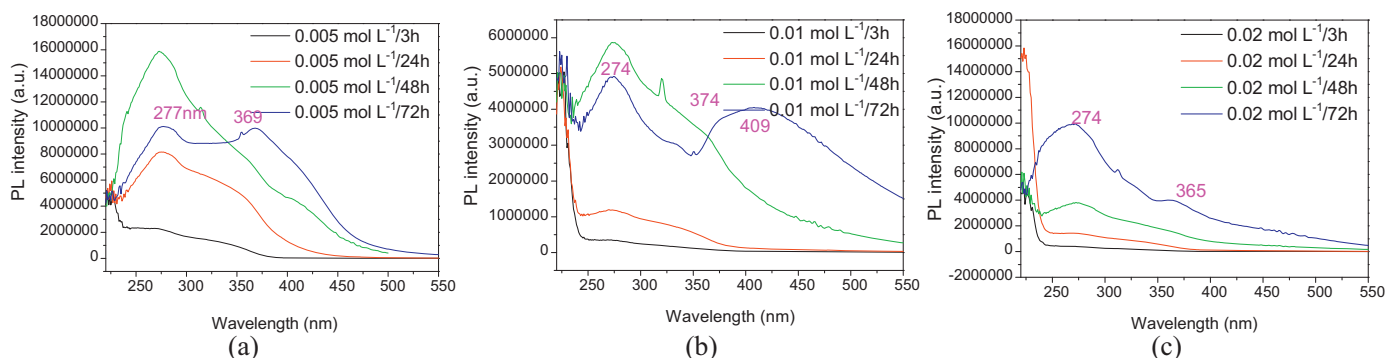


Fig. 5. Excitation spectra of solid nanosponge-embedded Au_n clusters, for the study of temporal evolution of the core-etching for different initial HAuCl₄ concentrations.

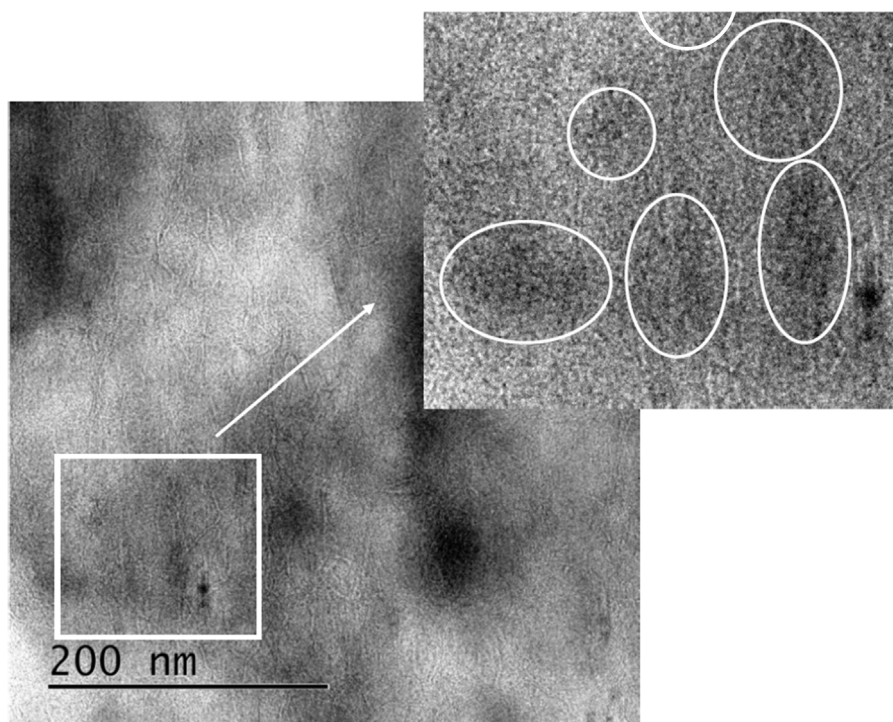


Fig. 6. TEM image of nanosponge-embedded Au_n clusters.

18 min with no induction time, in contrast to several other reports. Yamamoto et al. (2012) listed the main causes for induction time, including diffusion of the reactant molecules to the active sites and restructuring of surface atoms of the nanoparticles, thus none of this happened here. This is an important point since, as it has been evidence by Shibu and Pradeep (2011) from two-dimensional ROESY 1H NMR spectra that the Au_{15} clusters are included in the CD cavities without losing their capping GSH layer. Nevertheless the cluster surface remains readily available in the nanosponge with no steric hindrance to 4NP molecules.

As shown by Wunder, Polzer, Lu, Mei, and Ballauff (2010), this model reaction generally follows Langmuir–Hinshelwood kinetics

with adsorption of both reactants on the catalyst surface. According to this model a plot of $-\ln(C/C_0)$ versus t should be a straight line for which the slope is related to the rate constant. The curve equation was $y = -0.016 + 0.002x$ ($R = 0.991$), then the rate constant was $2 \times 10^{-3} s^{-1}$. Compared to previous data it is on the same order of magnitude: Yamamoto et al. (2012) obtained a value of $3 \times 10^{-3} s^{-1}$ for DMF-stabilized AuNC and of $8 \times 10^{-3} s^{-1}$ for the well known $Au_{25}(SG)_{18}$ cluster. As we found a rate constant in the same magnitude order as aqueous suspensions of analogous Au_n clusters this indicates that the immobilization into β -CD cavities on the solid phase did not impaired the catalytic activity of the material but improved the catalyst processability after the process.

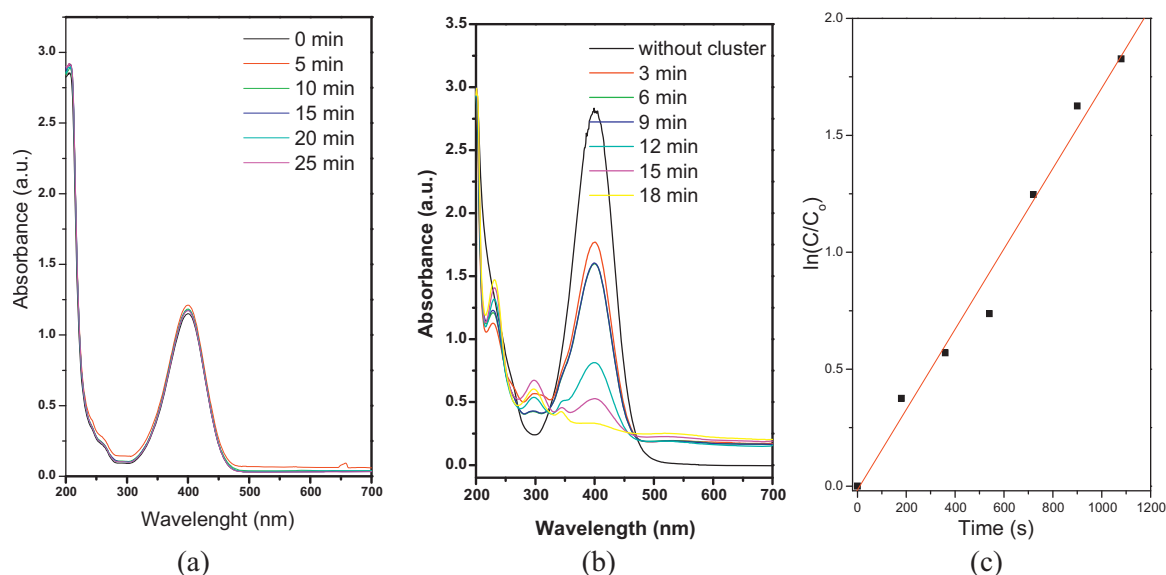


Fig. 7. Evolution of the absorption spectra in solution containing 4NP with time in the presence of: (a) the parent nanosponge; (b) nanosponge-embedded Au_n clusters; (c) plot of the Langmuir–Hinshelwood kinetic model.

4. Conclusions

The β -CD bound to a polymer network (nanosponge) were still able to act as templates to the generation of Au_n clusters by core-etching of precursor Au nanoparticles. The proportion of nanosponge during core-etching process plays a significant role as it allowed faster loading of $\text{Au}_{11}/\text{Au}_{15}$ clusters as well as a higher cluster loading in the nanosponge. Finally, the catalytic activity of the Au_n clusters was found to be in the same magnitude order than similar cluster suspensions.

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