J. Mater. Environ. Sci. 4(6) (2013) 1013-1018
ISSN : 2028-2508
CODEN: JMESCN

Sunlight- mediated synthesis of silver nanoparticles using honey and its promising anticorrosion potentials for mild steel in acidic environments

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Received 22 Jan 2013, Revised 25 May 2013, Accepted 25 May 2013
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Abstract
We have developed a simple, novel, green, sunlight mediated and economically feasible approach for the synthesis of silver nanoparticles (AgNPs) using a bio-derived product-honey. AgNPs was characterized using UV-Vis absorption spectrophotometer. An intense surface plasmon resonance band at 450 nm in the UV–visible spectrum clearly revealed the formation of the silver nanoparticles. The effect of the synthesized nanoparticles on the corrosion of mild steel in 0.5 M HCl was studied by electrochemical methods. The experimental results suggest that the silver nanoparticle from honey is an effective corrosion inhibitor for mild steel.
Keywords: Honey; Silver nanoparticles; Mild steel; Corrosion; Hydrochloric acid.

Introduction
One of the most promising and recent areas of research in modern science is nanotechnology [1]. The major thrust has been developing new materials and examining their properties by tuning the particle size, shape and distribution. Metal nanoparticles have been extensively studied due to their specific characteristics such as catalytic activity [2] optical properties [3], electronic properties [4], antimicrobial properties [5], electrochemical properties [6], and corrosion inhibition properties on iron and copper [7, 8].

The use of chemical and physical method in the synthesis of nanoparticles is very expensive and cumbersome. The chemical and physical methods of nanoparticle synthesis lead to the presence of some toxic chemicals absorbed on the surface that may have adverse effects in their applications. Therefore, there is a growing need to develop environmentally benign nanoparticles. Researchers have used biological extracts for the synthesis of nanoparticles by adopting simple protocols, involving the process of reduction of metal ions by using biological extracts as a source of reductants either extracellularly or intracellularly [9-11]. Synthesis of nanoparticles may be triggered by several compounds such as carbonyl groups, terpenoids, phenolics, flavonones, amines, amides, proteins, pigments, alkaloids and other reducing agents present in the plant extracts and microbial cells [12].

The major drawback of producing nanoparticles using plants and microbial cells is the long hours required for the synthesis and the high energy cost (temperature) involved [13]. In recent times, honey has been reported as effective corrosion inhibitor for carbon steel [14], copper [15], tin [16], duplex stainless steel [17], aluminium alloy in seawater [18], CuNiFe alloy in sodium chloride solution [19], Al-Mg-Si alloy in seawater [20], and Q235 steel in simulated brine [21]. The exploitation of honey in the field of nanotechnology to developed cost effective and environmentally benign synthesis of nanoparticles have been well documented [22 -24], but the use of sunlight mediated approach for the synthesis of silver nanoparticles from natural honey has not been reported in the literature. Honey is a natural food produced by bees from nectar or secretion of flowers. Honey has a content of 80-85 % carbohydrates, 15-17 % water, 0.3 % proteins, 0.2 % ashes, and minor quantities of amino-acids and vitamins as well as other components in low levels of concentration [25]. According to Venu et al. [24], honey mediated biological synthesis has advantages over other types of biological methods, including avoiding of the elaborate processes such as drying plant materials and maintenance of cell cultures.

In this paper, we have exploited natural honey and sunlight irradiation for facile and fast synthesis of silver nanoparticles. The honey serves as both reducing and capping agent. No other intermediate stabilizing agent was added. The water-soluble and highly-dispersed colloidal silver nanoparticles was stable for more than 6 months. Furthermore, the silver nanoparticles synthesized were characterized using UV-Visible absorption spectrophotometer and thereafter tested for the first time as corrosion inhibitor for mild steel in hydrochloric acid solution using electrochemical techniques. The silver nanoparticles broth from honey gave excellent protection to steel against corrosion in acidic solution.

2. **Materials and methods**

2.1. Chemicals and materials

$AgNO_3$ and HCl of analytical grade were purchased from Sigma Aldrich. Natural honey used in this study was obtained from the Department of Pharmacy, University of Uyo, Nigeria.

2.2. Synthesis of silver nanoparticles

For the reduction of silver ions, 5 ml of honey was added to 95 mL of 0.1 M aqueous $AgNO_3$. The reaction mixture was stirred properly and exposed to bright sunlight. Within seconds of exposure to sunlight the solution turned to yellowish-brown indicating the formation of of silver colloid (Fig. 1) [23]. The intensity of colour increased with increasing time and remained unchanged after 10 minutes.

Fig. 1. Left: Pure honey; Right : Silver nanoparticle (AgNPS) from honey.

2.3. Characterization

UV-vis spectroscopic analysis of the yellowish-brown coloured solution was carried out using Lambda 2 spectrophotometer Perkin-Elmer. The samples were analyzed by preparing dilute solutions of the silver nanoparticles in distilled water. The reduction of silver ions was monitored from (350 – 650) nm.

2.4. Electrochemical measurements

Metal samples for electrochemical experiments were machined into test electrodes of dimension 1 x 1 cm and fixed in polytetrafluoroethylene (PTFE) rods by epoxy resin in such a way that only one surface, of area 1 cm^2, was left uncovered. The exposed surface was cleaned using the procedure as earlier described [8]. Electrochemical experiments were conducted in a conventional three-electrode glass cell of capacity 400 mL using a VERSASTAT 400 Complete DC Voltammetry and Corrosion System, with V3 Studio software. A graphite rod was used as counter electrode and a saturated calomel electrode (SCE) as reference electrode. The latter was connected through a Luggin's capillary. Measurements were performed in naturally aerated and unstirred solutions at the end of 1 h of immersion at 303 K. Impedance measurements were made at corrosion potentials (E_{corr}) over a frequency range of 100 kHz–10 mHz, with a signal amplitude perturbation of 5 mV. Potentiodynamic polarization studies were carried out in the potential range ±250 mV versus corrosion potential at 0.333 mV/s scan rate. The aggressive solution of 0.5 M HCl was prepared by dilution of AR grade 37% HCl with distilled water. The concentration range employed for silver nanoparticles (AgNP) was 2 – 6 % (v/v).

3. Results and discussion

3.1. *UV- Visible spectroscopy*

UV-Visible spectroscopy is one of the most widely used techniques for the stuctural characterization of silver nanoparticles [23, 24]. Metallic nanoparticles display characteristic optical absorption spectra in the UV–visible region called surface plasmon resonance (SPR). The physical origin of light absorption of metallic nanoparticle is the coherent oscillation of conduction electron induced by the interacting electromagnetic field [26]. When a small spherical metallic nanoparticle is irradiated by light, the oscillating electric field causes the oscillation of conduction electron to oscillate coherently. When electron cloud is displaced relative to the nuclei a restoring force initiates a coulomb attraction between electrons and nuclei that results in oscillation of electron cloud relative to the nuclear framework. These resonance is known as SPR and are actually small particle effect since they are absent in their individual atom, as well as in their bulk.

Figure 2 shows UV-Vis spectra recorded from the reaction medium after 48 hours. Absorption spectra of silver nanoparticles formed in the reaction media has absorbance peak at 450 nm. The broadening of the peak at that wavelength is attributed to the formation of polydispersed silver nanoparticles [27].

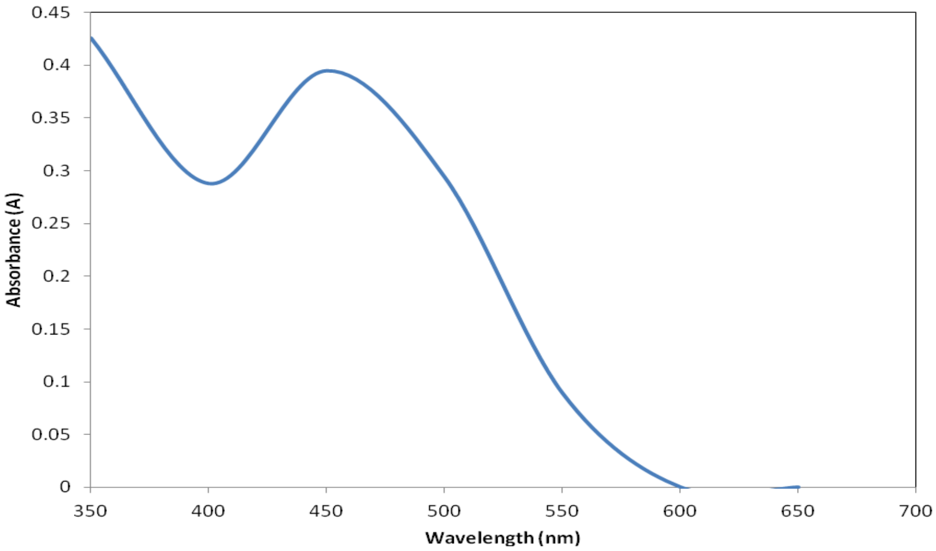

Fig. 2. UV–vis spectra of honey containing AgNPs.

3.2. *Potentiodynamic polarization measurements*

Polarization measurements are suitable for monitoring the progress and mechanisms of the anodic and cathodic partial reactions as well as identifying the effect of an additive on either partial reactions. Potentiodynamic polarization experiments were thus carried out to understudy the effect of adsorbed silver nanoparticles on the kinetics of the anodic and cathodic processes. The potentiodynamic polarization curves of mild steel in 0.5 M HCl solution with various concentrations of silver nanoparticles (AgNPs) are shown in Fig. 3. Inspection of the plots reveal that the mild steel specimen exhibit active dissolution with no distinctive transition to passivation within the studied potential range in all environments. Electrochemical polarization parameters such as corrosion potential E_{corr} (mV, SCE), corrosion current density i_{corr} (μA cm^{-2}), cathodic and anodic Tafel slopes-β_c and β_a, (mV dec^{-1}) and inhibition efficiency (*I %*) values are given in Table 1. The *I %* was calculated from polarization measurements according to the relation equation given below:

$$I\% = \left(\frac{i_{corr} - i^{*}_{corr}}{i_{corr}} \right) \times 100 \qquad (1)$$

where i_{corr} and i^*_{corr} are the uninhibited and the inhibited corrosion current densities, respectively. It is clear from Fig. 3 that both the anodic metal dissolution and cathodic hydrogen evolution reactions were inhibited after the addition of AgNPs to the aggressive medium. The inhibitions of these reactions are more pronounced with the increasing inhibitor concentration while the corrosion potential values shifted to more positive values. These results indicate that AgNPs acts as the mixed type corrosion inhibitor. The inhibitor molecules are first adsorbed on the mild steel surface by blocking the available reaction sites. The inhibition efficiency increase with increasing inhibitor concentrations reaching a maximum of 91.5 % at a concentration as low as 6 % v/v of AgNPs.

Table 1. Corrosion parameters obtained by polarization measurements for mild steel sample in 0.5 M HCl with different concentrations of AgNPs from honey at 303 K.

Concentration (% v/v)	E_{corr} (mV/SCE)	I_{corr} (μA cm^{-2})	β_c (mV dec^{-1})	β_a (mV dec^{-1})	I%
0	-529.72	550.78	99.67	158.57	-
2	-502.64	118.82	40.13	54.61	78.4
4	-495.91	80.53	42.93	64.91	85.3
6	-486.94	46.37	42.76	59.04	91.6

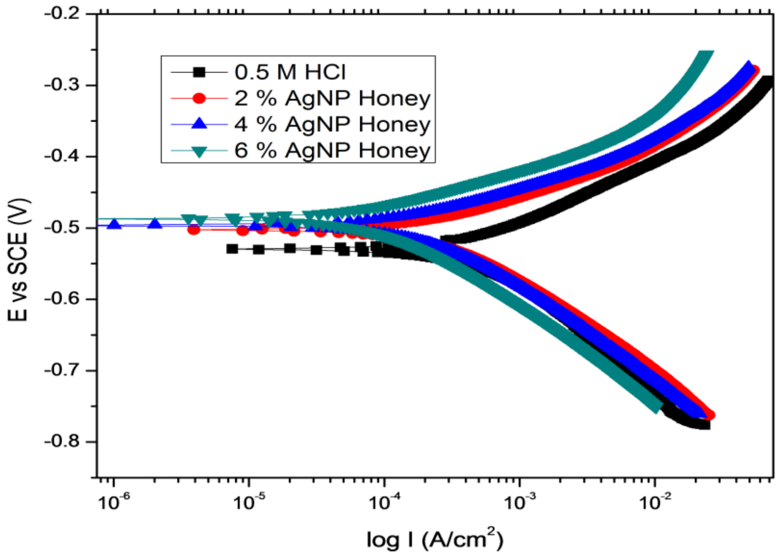

Fig. 3. Polarization curves for mild steel in 0.5 M HCl containing different concentrations of AgNPs from honey

3.3. *Electrochemical impedance spectroscopy (EIS)*

Impedance experiments were undertaken to gain insight into the characteristics and kinetic of electrochemical processes occurring at the steel/acid interface in the absence and presence of AgNPs. The impedance responses of these systems are given in Figure 4 in Nyquist modulus format. The complex impedance diagram recorded at E_{corr} in the absence and presence of varying concentrations of AgNPs has similar shape, indicating that almost no change in the corrosion mechanism occurred as a result of AgNPs addition. The Nyquist plots generally comprise of only one depressed capacitive semicircle in the high frequency region, which corresponds to one time constant. Inspection of Fig. 4 also reveals that increase in concentration of AgNps results in increase in size of the semicircle which is an indication of the inhibition of the corrosion process. It is observed that capacitive semicircles in the absence and presence of AgNPs were depressed with centre under the real axis. This kind of behaviour is typical of solid metal electrodes that show frequency dispersion [28]. When a non ideal frequency is present, the capacitor is replaced by a constant phase element (CPE). The CPE is usually used to compensate for the deviations from ideal dielectric behaviour and is related to surface inhomogeneities. The impedance, Z, of CPE is given as:

$$Z_{CPE} = Q^{-1}(j\omega)^{-n} \qquad (2)$$

where Q and n represents the CPE constant and exponent respectively, j = $(-1)^{½}$ is an imaginary number and ω is the angular frequency in rad s^{-1} (ω = 2πf), where f is the frequency in hertz. The parameter n is generally accepted to be a measure of surface inhomogeneity.

The impedance spectra for the Nyquist plots were analyzed using the equivalent circuit model $R_s(Q_{dl}R_{ct})$, which has been reported in the literature to be previously used to model the Fe/acid interface [29-37]. Of the electrochemical parameters obtained, our interest was on the charge transfer resistance (R_{ct}) which was used to compute the corrosion inhibition efficiency using the expression:

$$I\% = \left(\frac{R_{ct} - R_{ct}^{o}}{R_{ct}} \right) \times 100 \qquad (3)$$

where R^{o}_{ct} and R_{ct} are uninhibited and inhibited charge transfer resistance respectively.

The value of I % obtained at the highest concentration of AgNPs (6 % v/v) was found to be 93.1% and compares favourably with the value obtained for potentiodynamic polarization measurements.

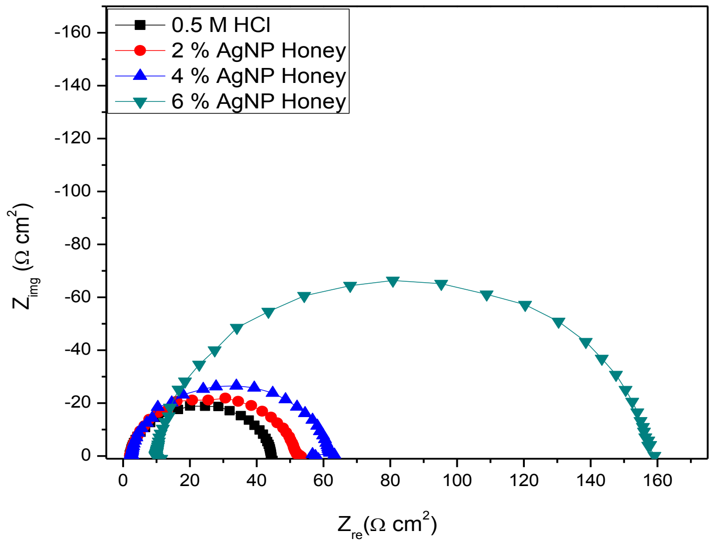

Fig 4. Nyquist plots of mild steel in 0.5 M HCl containing different concentrations of AgNPs from honey.

4. Conclusions

A completely green and fast method for the synthesis of silver nanoparticles using honey and sunlight is reported for the first time. The method is fast as opposed to the slow reduction kinetics reported in other studies using biosynthetic routes for synthesizing Ag nanoparticles. Light was used as constructive agent for the synthesis of silver nanoparticles in the aqueous medium containing 0.1 M $AgNO_3$ and honey. The synthesized nanoparticles remained stable at room temperature for more than six months. The possible reducing agent is fructose and capping material responsible for stabilization is proteins present in honey. Silver nanoparticles synthesized by the reported method are found to have excellent corrosion inhibition potentials on steel in 0.5 M HCl.

5. Future work

FT-IR, SEM-EDX, XRD, TEM and other surface analytical techniques will further be used to characterze the silver nanoparticles and to study in detail the surface morphology of the steel surface with and without AgNPs in the acidic medium. This will aid in proposing a suitable mechanism for the inhibition of the AgNPs on steel surface.

Acknowledgements-TWAS, the Academy of Sciences for the Developing World, is gratefully acknowledge for Grants for Research Units in Developing Countries Program (10−107RG/CHE/AF/AC-G).

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(2013) ; http://www.jmaterenvironsci.com