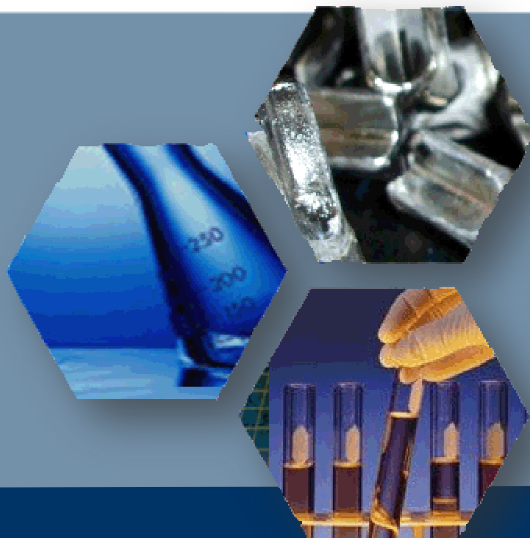
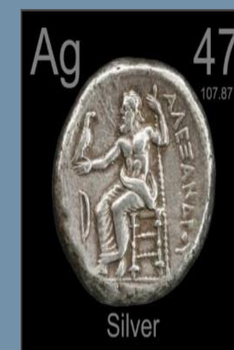
Production of highly dispersed silver nanoparticles recovered from photographic film wastes using a simple green method





22nd March 2015

by

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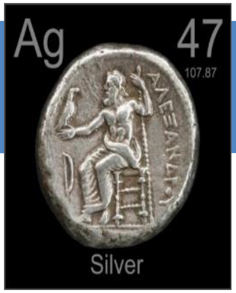
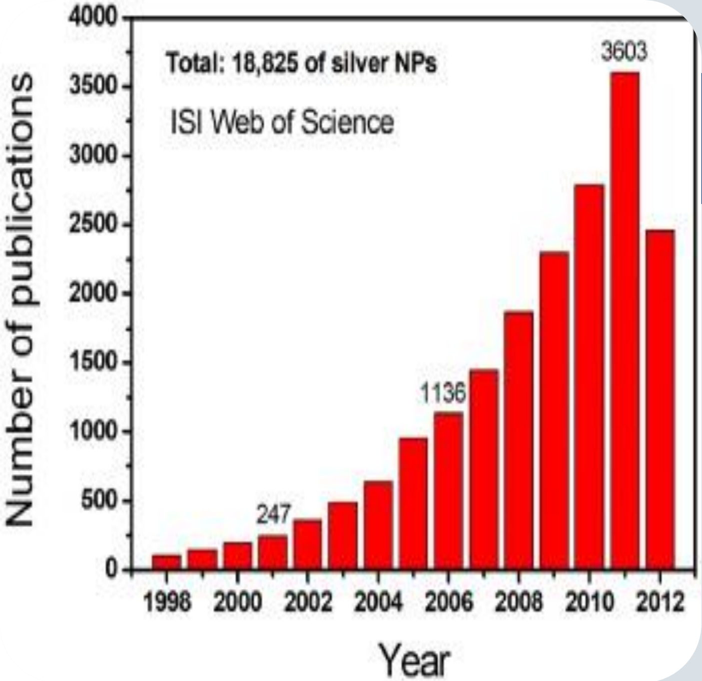
Points of interest

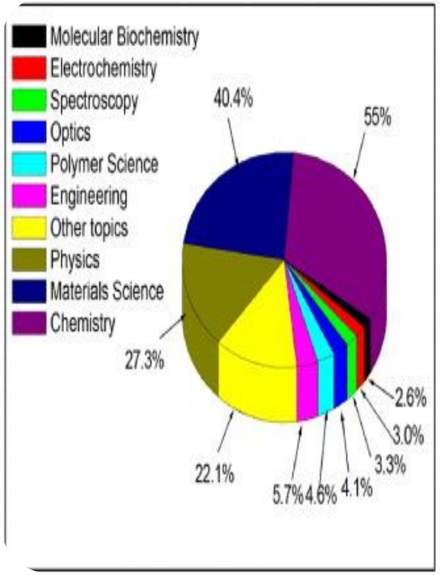
- Introduction to nanomaterials
- Challenges.
- Aim of work.
- Preparation and Charecterization of Silver Nanoparticles(AgNPs).
- Application of AgNPs.
- Conclusion.

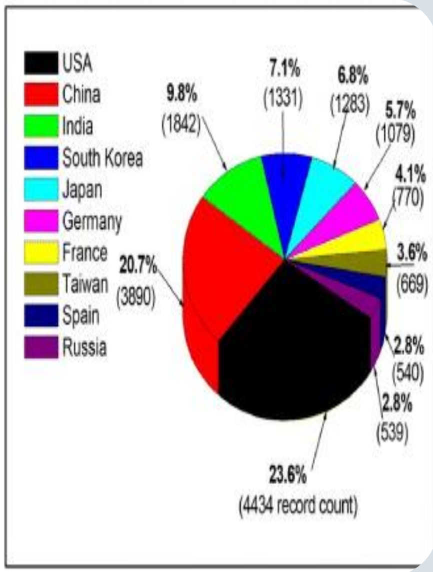
Why Silver?



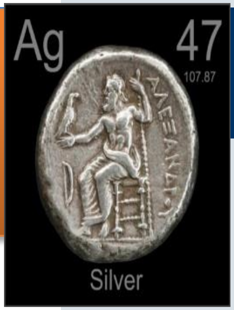
- Effectiveness in killing a wide range of bacteria.
  - Including some of the strains that have proven resistant to moder n antibiotics
- Can be readily incorporated into plastics, fabrics and onto surfaces
- Delivers toxic silver ions in large doses directly to sites where they most effectively attack microbes

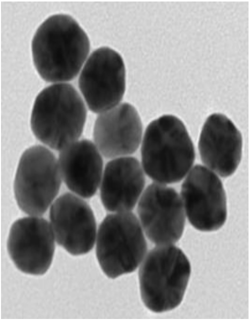






Why do we concern with AgNPs ?





- High efficacy in killing a wide range of bacteria, especially some species of bacteria that have proven resistance to modern antibiotics.
- The anticancer action of silver nanoparticles.
- Anti corrosive properties of nanocomposites based AgNPs.

Cautions

Approximately 2 billion radiographs are taken around the world each year, including chest X-rays, mammograms, CT scans, etc. Traditionally, 94-98% of X-ray films are used in medical services.

A review of recovery of metals from industrial waste
U.U. Jadhav, H. Hocheng, *Journal of Achievements in Materials and Manufacturing Engineering, Volume 54 Issue 2 October 2012*

Recovery the silver from waste

(a) burning the films directly.

(b) oxidation of the metallic silver following electrolysis, and

(c) stripping the gelatine-silver layer using different solutions. (nitric acids, oxalic acid, hydrogen peroxides

Therefore there is a need to develop cost effective and environmentally friendly methods to recover silver from X-ray/photographic waste.

P. K. Giri et al. (eds.), Advanced Nanomaterials and Nanotechnology, 143, DOI: 10.1007/978-3-642-34216-5_7,

Previous work

A new method for the preparation of silver nanoparticles (AgNPs) on silver chloride using hydrazine as reducing agent
Rao GP, Yang J. Appl Spectrosc. 2010 Oct;64(10):1094-9. doi: 10.1366/000370210792973640.

A Novel Silver Recovery Method from Waste Photographic Films with NaOH Stripping
N. NAKIBOGLU, et al., Turk J Chem 27 (2003) , 127- 133.

Silver recovery from synthetic photographic and medical X-ray process effluents using activated carbon, (complex with thiosulfate)
K.G. Adani, R.W. Barley *, R.D. Pascoe, Minerals Engineering 18 (2005) 1269–1276

Enzyme extract obtained from *Bacillus subtilis* ATCC 6633 for silver recovery from the waste X-ray films. The enzymatic hydrolysis of the gelatin layers on the X-ray film enables not only the recovery of the silver, but also the polyester base which can be recycled.

N. Nakiboglu, D. Toscali, I. Yasa, Silver recovery from waste photographic films by an enzymatic method, Turkish Journal of Chemistry 25 (2001) 349-353.

Challenges

- Instability of AgNPs against HCl solutions.
- Tendency of free metal silver nanoparticles to form aggregates.
- High toxicity of AgNPs.
- Low yield of prepared AgNPs.
- Using of toxic capping and reducing agents in the preparation of AgNPs.

Aim of work

1. Recycling of silver from X-ray and photographic films

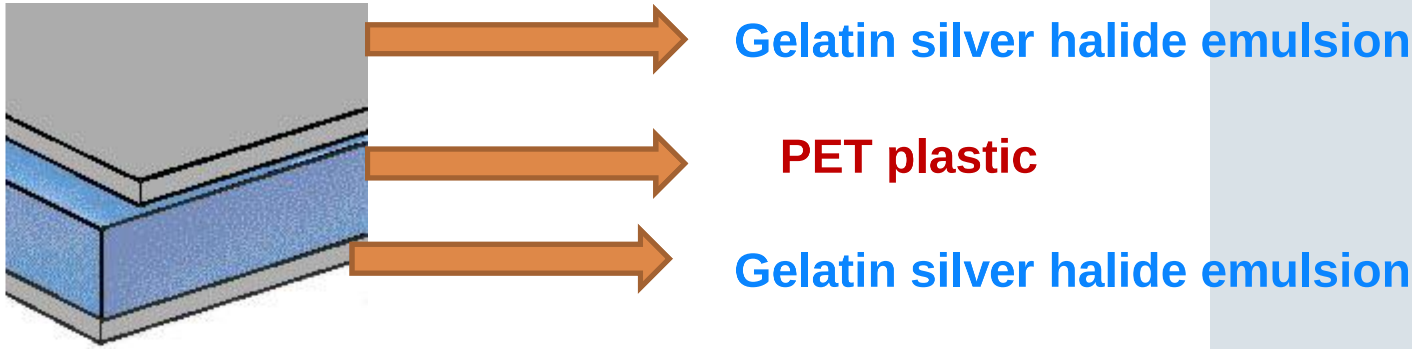
- glycose
- ammonia
- Sodium hydroxide

2. Properties of the produced AgNps

- Stability SSF
- Acid stability
- Corrosion inhibition

1. Synthesis and characterization of silver nanoparticles

Formation of silver nanoparticles



$$Ag^{+} + e^{-} \rightarrow Ag$$

Standard chemical potential -0.8 V

$$Ag_2O + H_2O + 2e^{-} \rightarrow 2Ag + 2OH^{-} \qquad E = 0.34\ V$$

$$2Ag^{+} + 2OH^{-} \rightarrow Ag_2O + H_2O$$

$$Ag^{+} + \tfrac{1}{2} C_6H_{12}O_6 + \tfrac{1}{2} H_2O \xrightarrow{\triangle} Ag + \tfrac{1}{2} C_6H_{11}O_7^{-} + \tfrac{3}{2} H^{+}$$

REACTION CONDITIONS

1- silver salts react with basic medium produce pure silver oxide.

2- reducing agent with alkaline can produce silver only

3- low pH can dissolve silver colloid

4- Gelatin and PVP optimize pH at 3

pH is important parameter for formation of silver

Gelatin can act as reducing and capping to control particle size

Temperature of reaction

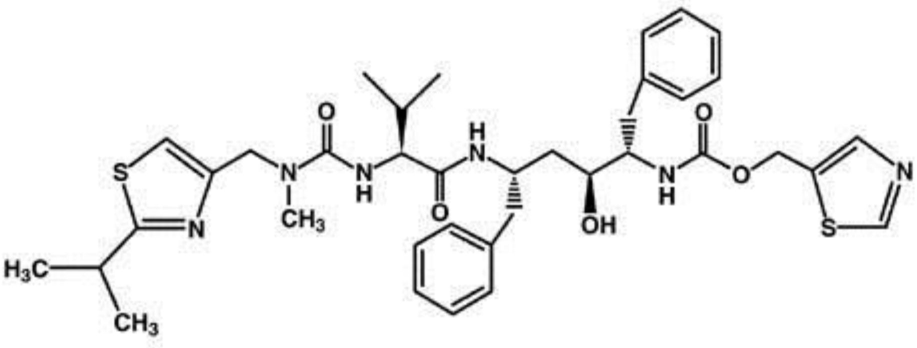
$$AgCl \rightarrow Ag^+ + Cl^-$$

$\downarrow$ Gelatin + OH- glucose

Ag0 capped gelatin

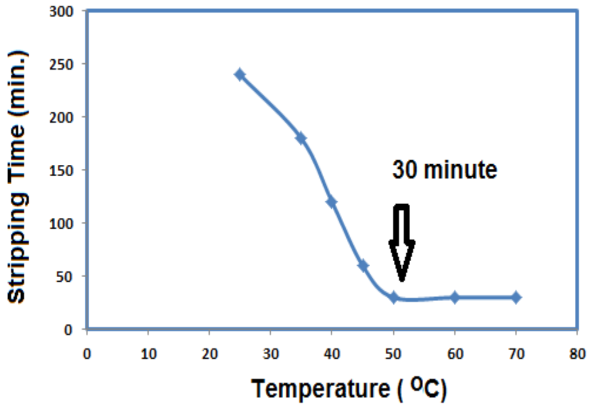
Gelatin

Gelatin is a protein which contains a large number of glycine, proline and 4-hydroxyproline residues.

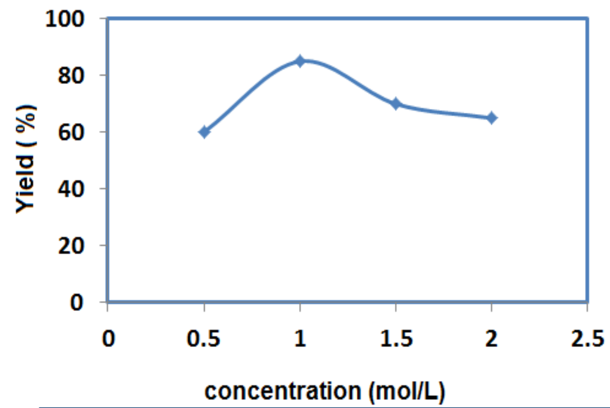


Reaction yields

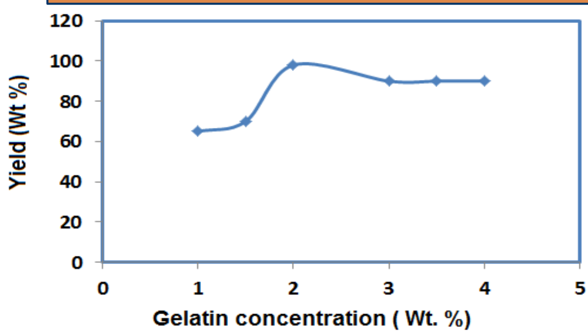
Silver stripping time



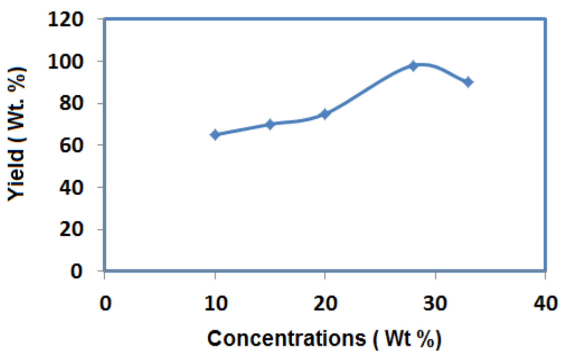
NaOH concentration



Gelatin concentration



Ammonia concentrations



Optimum reaction temperature 60 oC
Optimum glucose concentration 4 %

Characterization of AgNPs

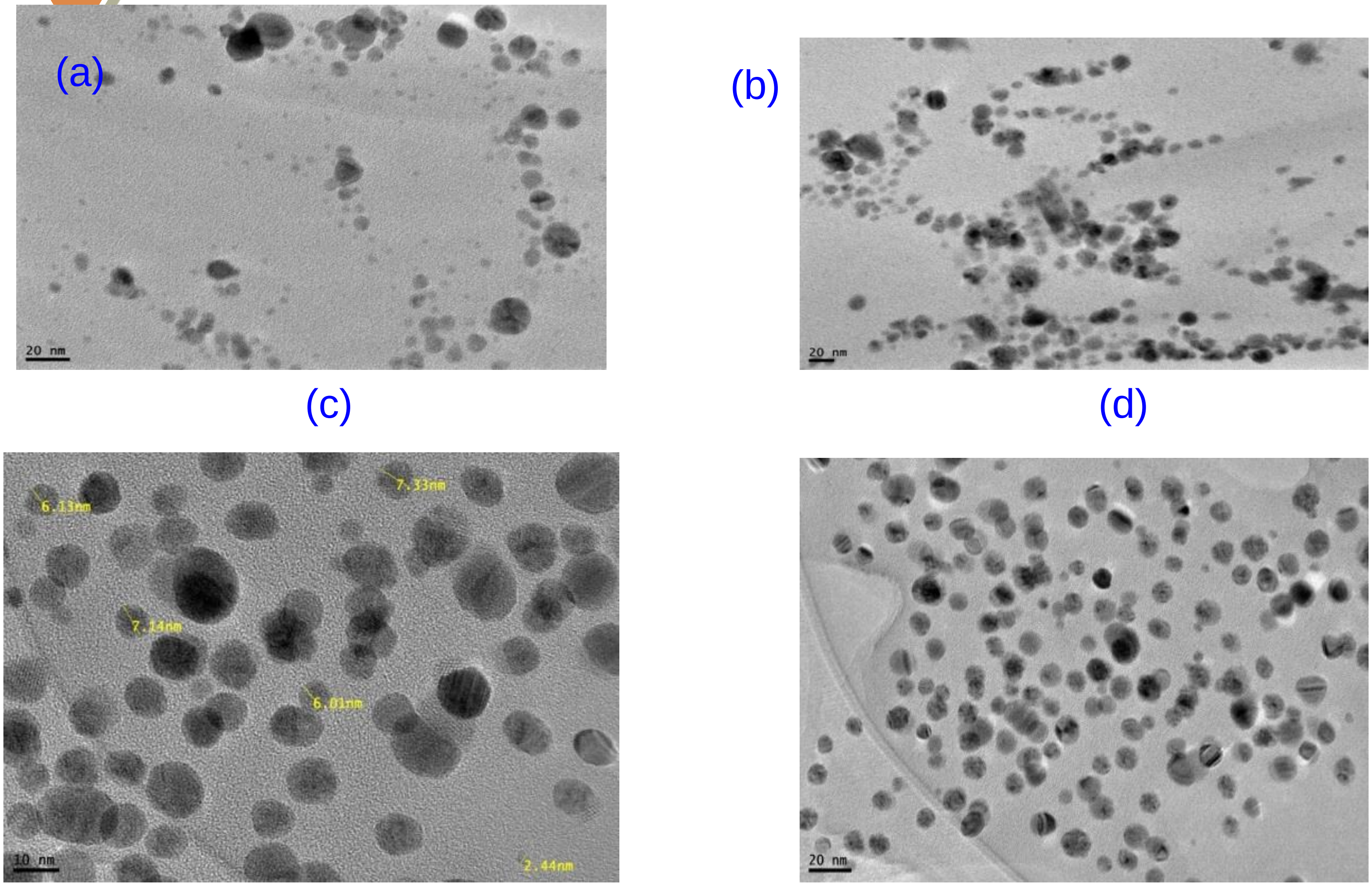


Figure6: TEM micrographs of AgNPs prepared with different amounts of PVASH a)0.5, b)1, c)2 and d) 3 (Wt %).

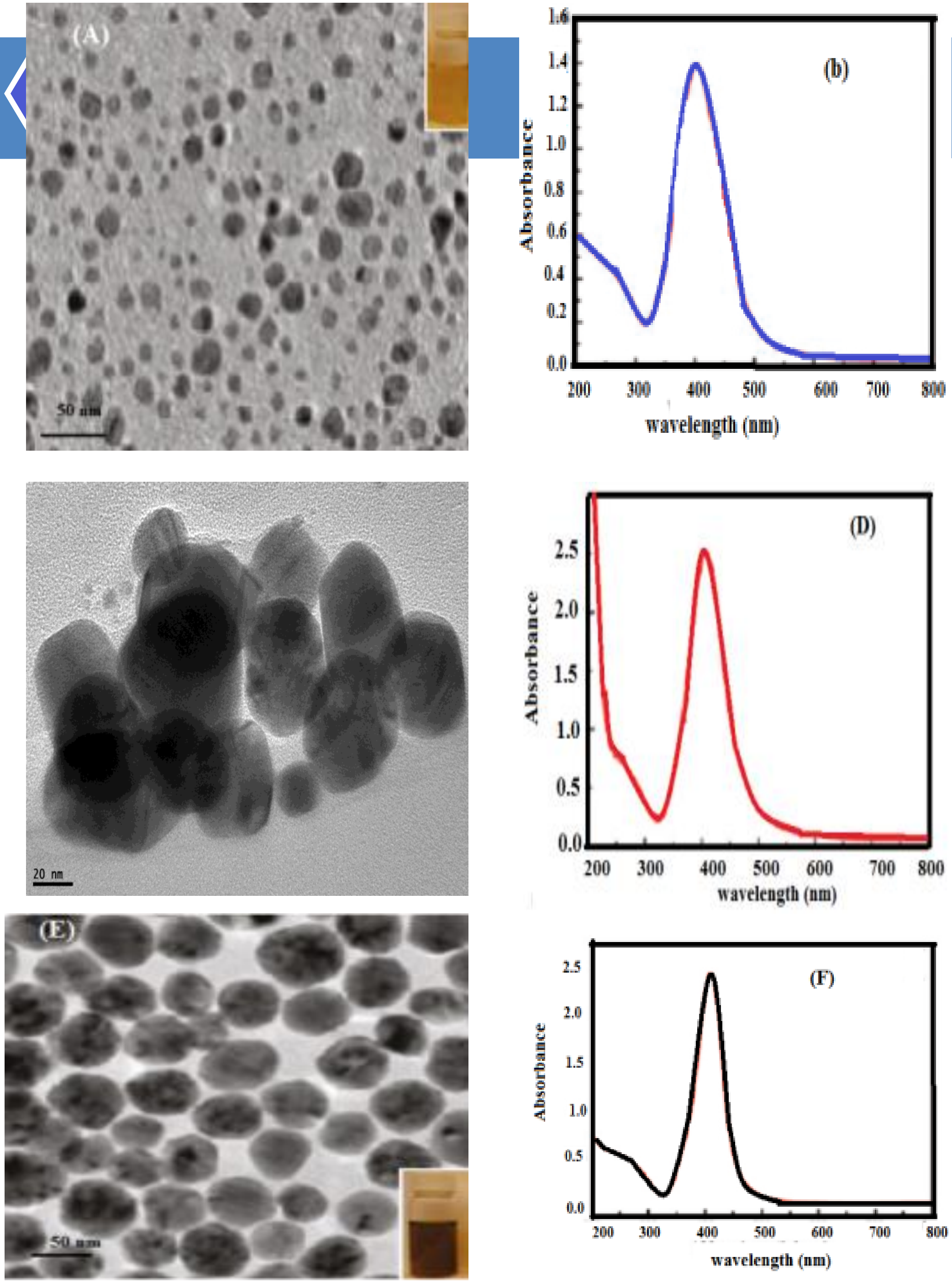
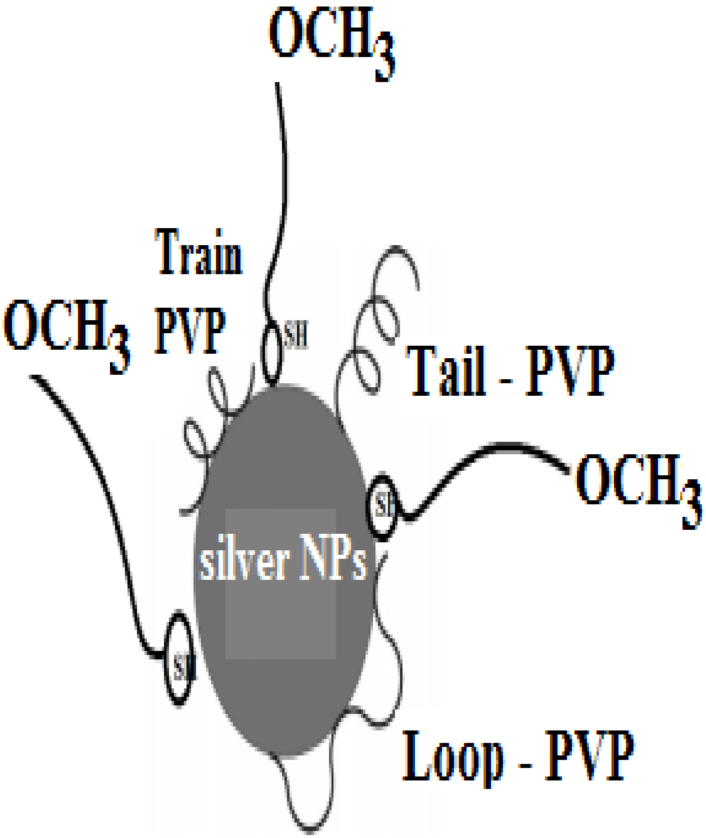


Figure 8. Set of images for Silver nanoparticles:
(A)TEM image of the citrate AgNP
(B) Its UV-vis absorption spectrum
(C)TEM image of PVP/PEGSH Ag NPs,
(D) its UV-vis absorption spectrum;
(E)TEM image of PEGSH Ag NPs and
(F)its UV-vis absorption spectrum.

Table 3.1: Average Diameters and Polydispersity Indices (PDI) Obtained from the PSDs Analyzed by TEM of the AgNPs.

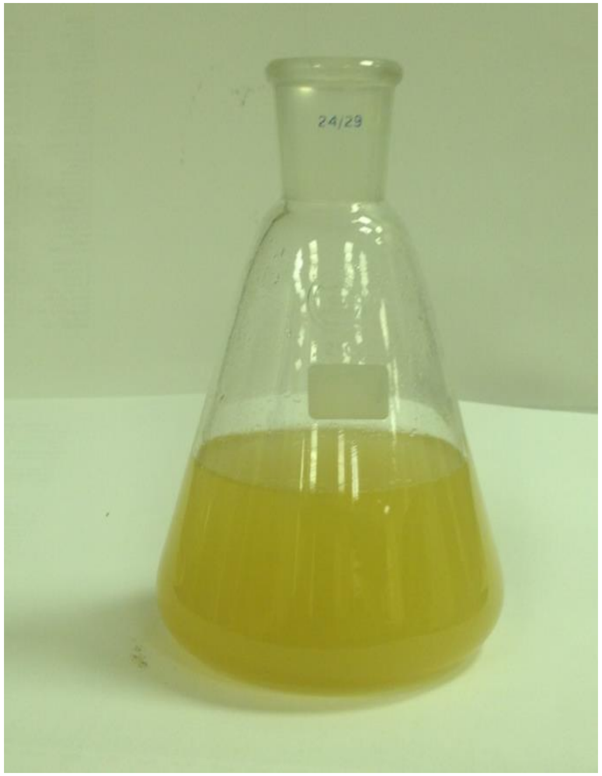
Sample	dn (nm)	dw (nm)	dv (nm)	PDI
Ag/citrate	5.6	10.9	6.15	1.920
Ag/PEGSH	10.9	16.2	12.3	1.476
Ag/PVP/PEGSH	27.7	28.3	27.9	1.081



scheme 4. Drafts of possible modes of how polymers can be bonded on the Silver NP surface.

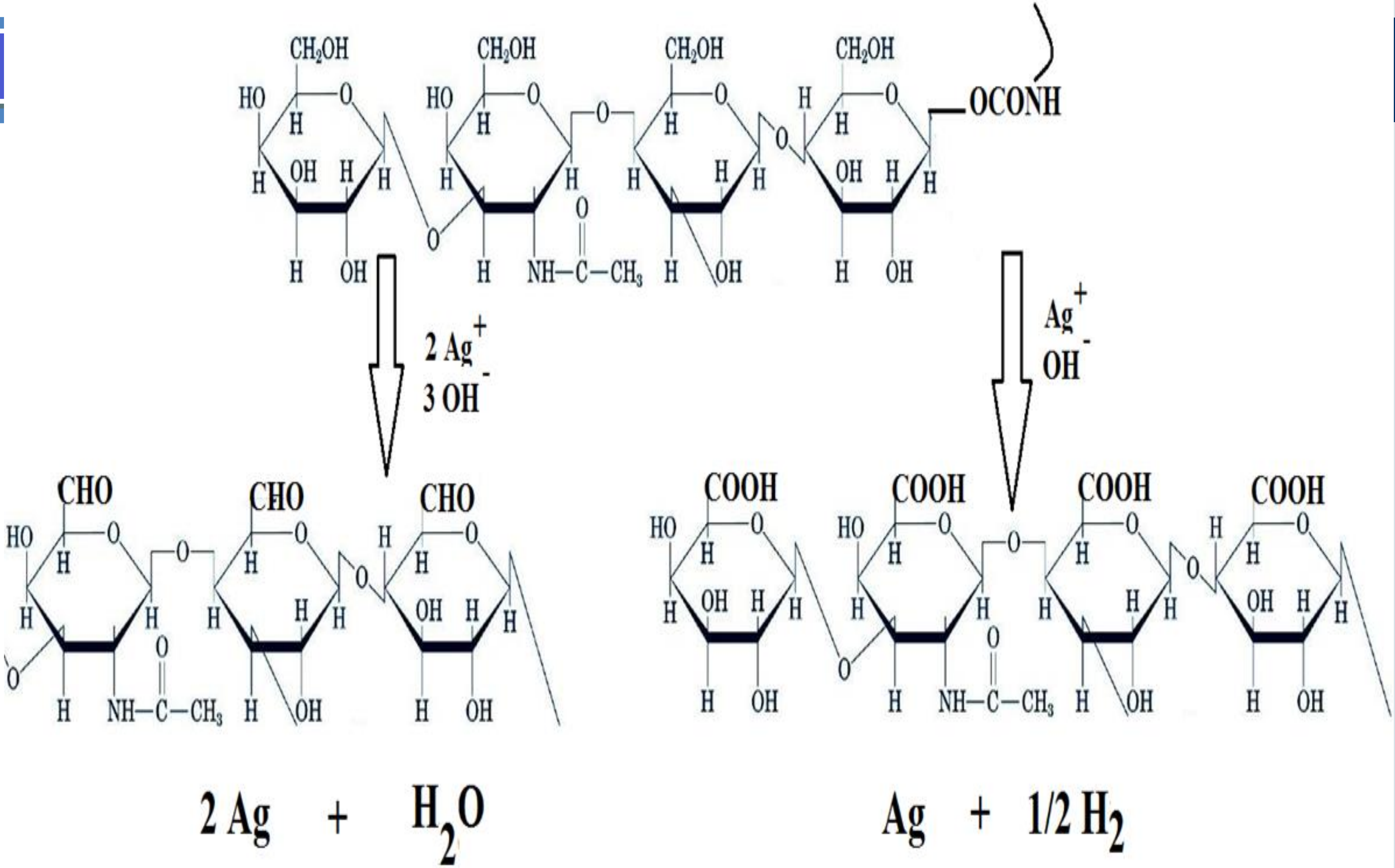
1.3 Capping of Silver nanoparticles with Murrh gum

Murrah as solid particles



Water extracted Murrh

AgNPS capped with Murrh



Scheme 5:Capping of silver nanoparticles with Murrh.

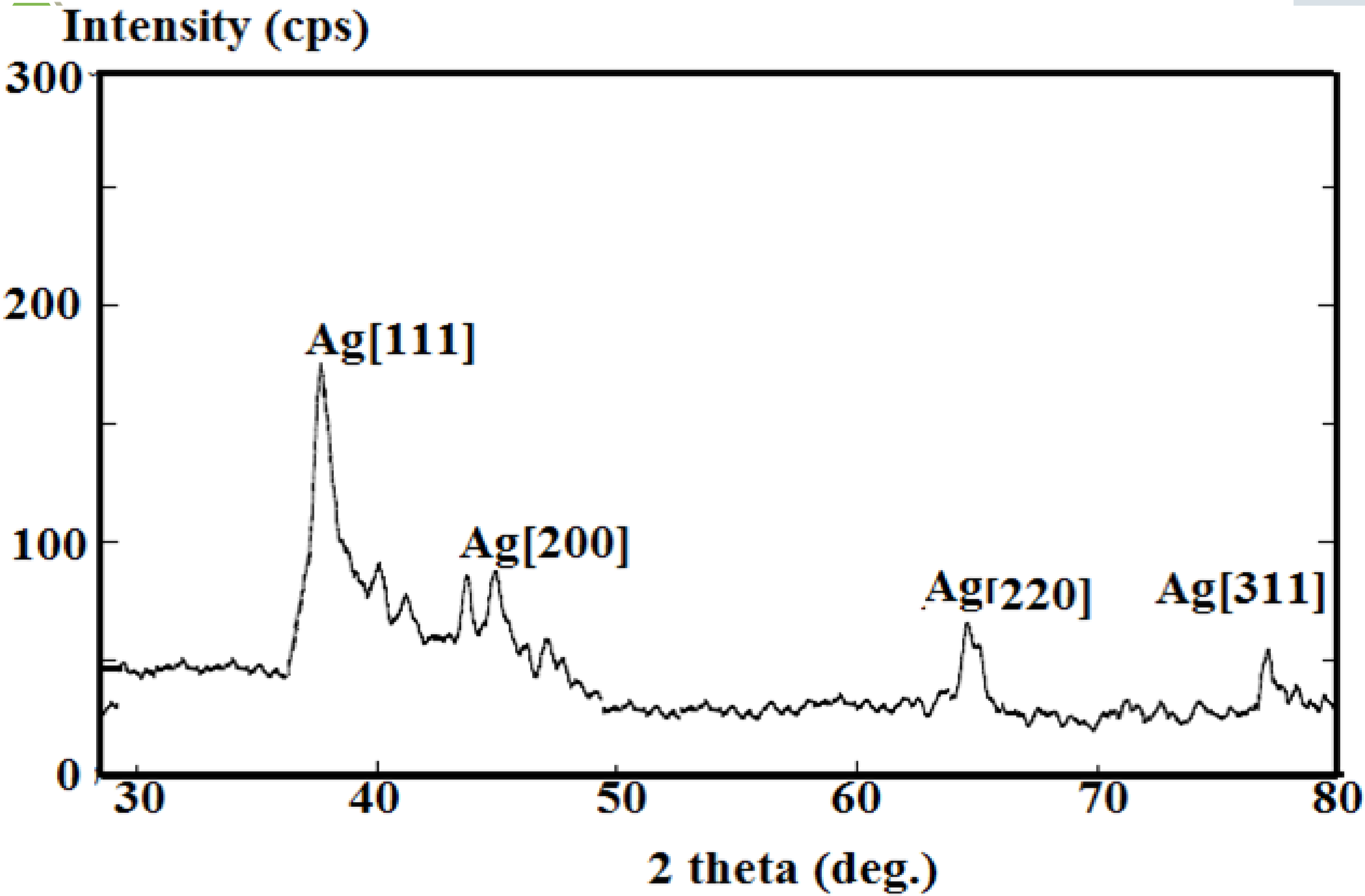


Figure 9: XRD patterns of AgNPs coated with Murrh.

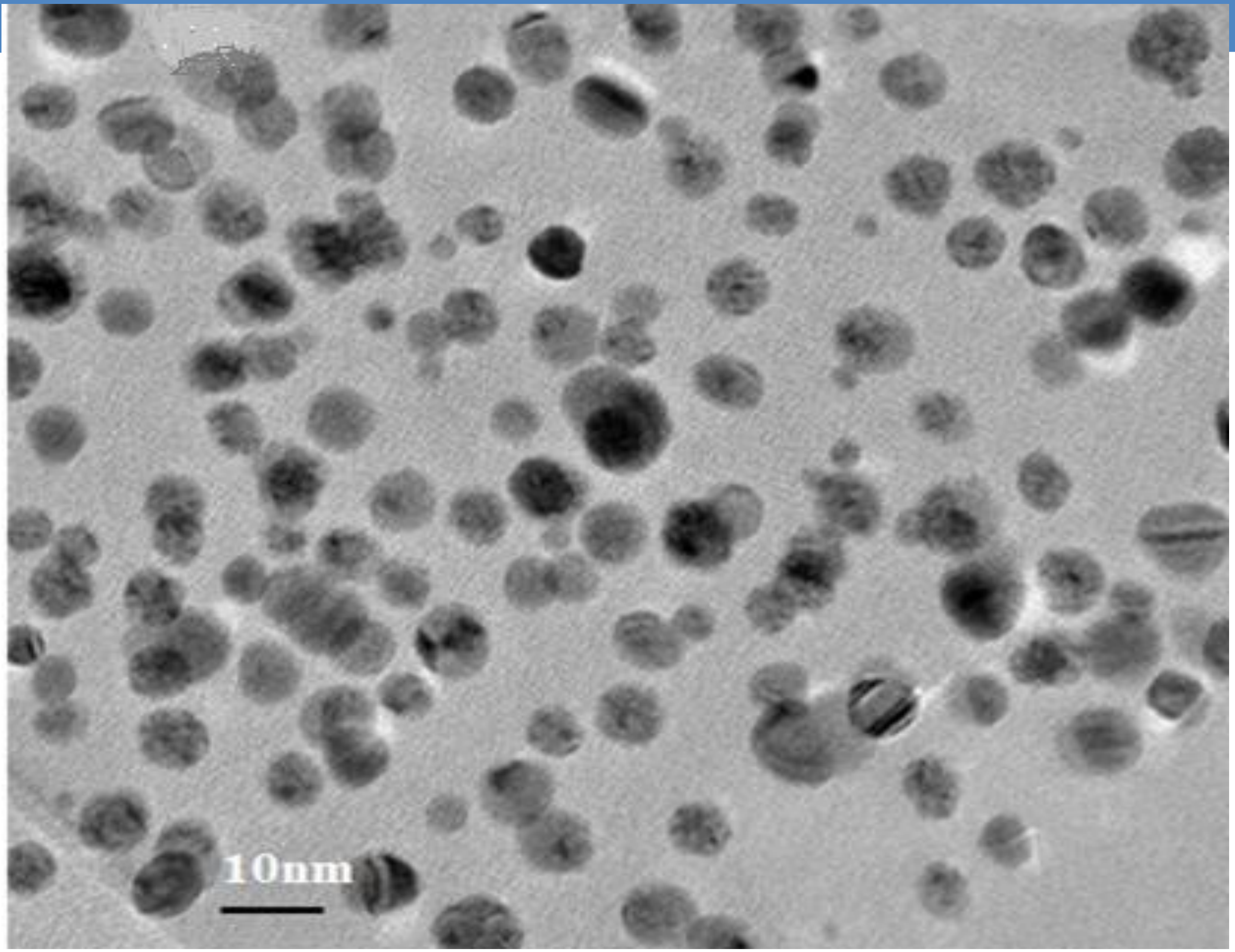


Figure 10: TEM micrographs of AgNPs coated with Murrh.

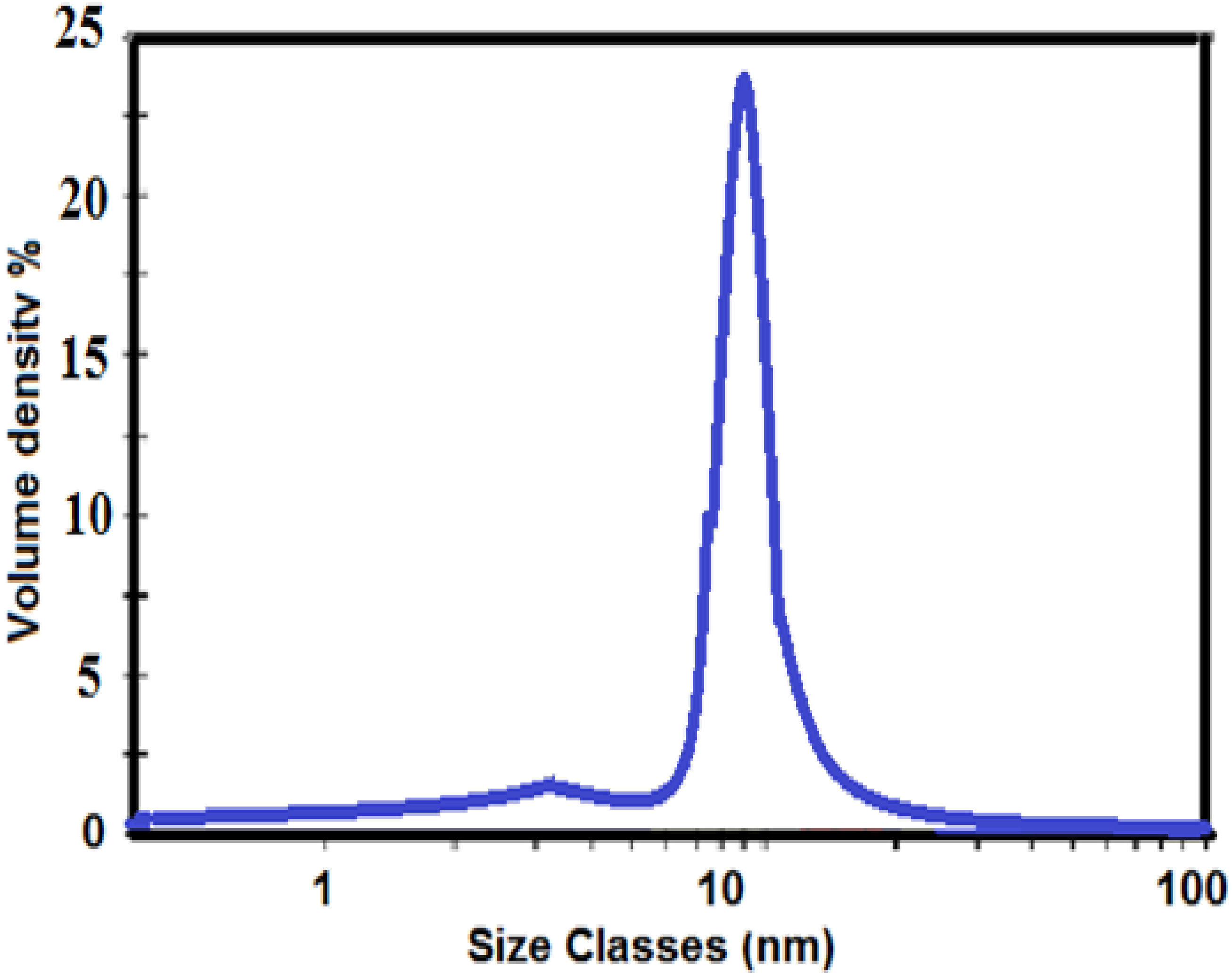


Figure 11. Particle size distribution of AgNPs coated with Murrh.

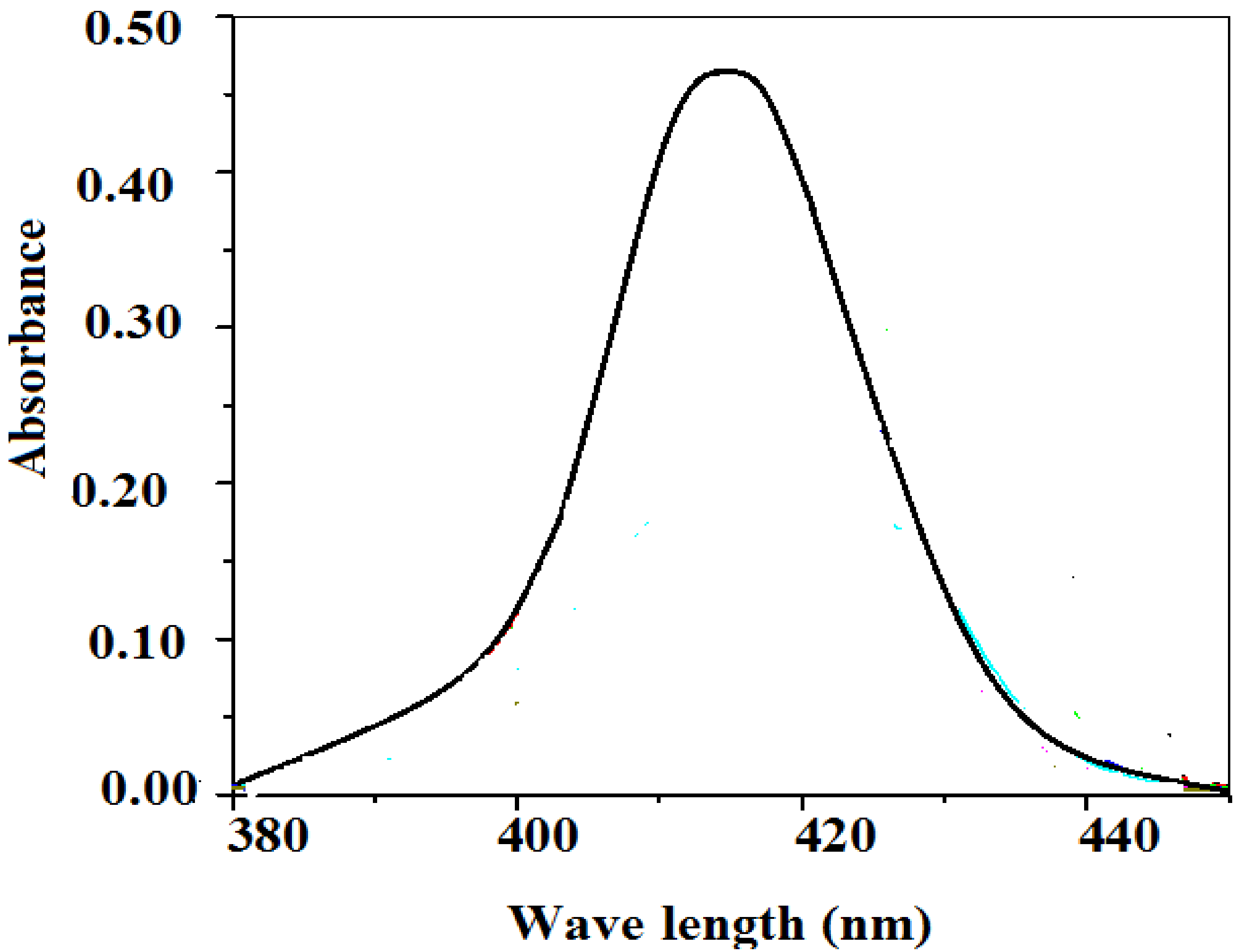


Figure 13: UV-Vis absorption spectra of Ag NPs coated with OA in hexane solution.

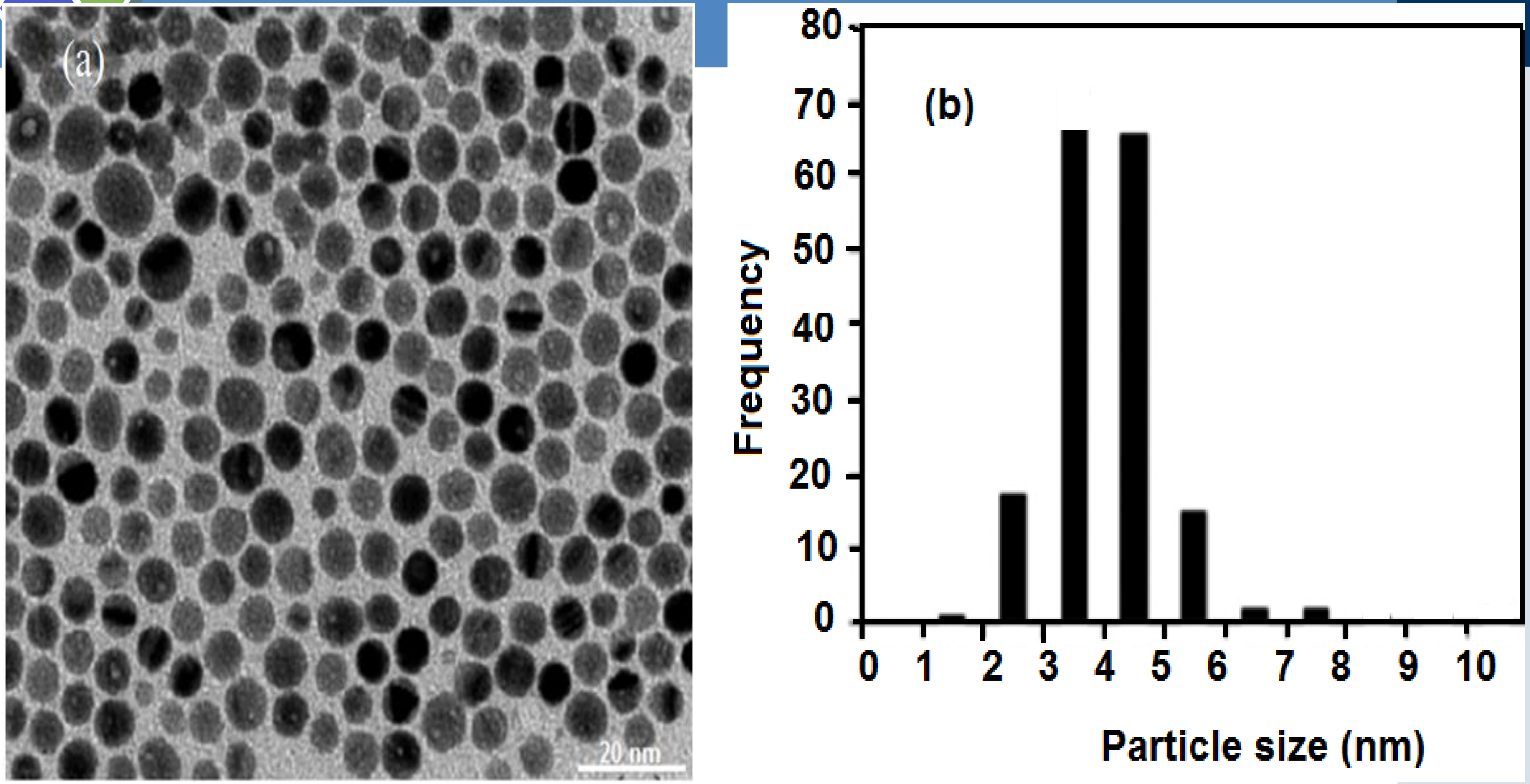


Figure 14: TEM micrographs of (a) Ag NPs capped with OA, (b) histogram of Ag NPs capped with OA.

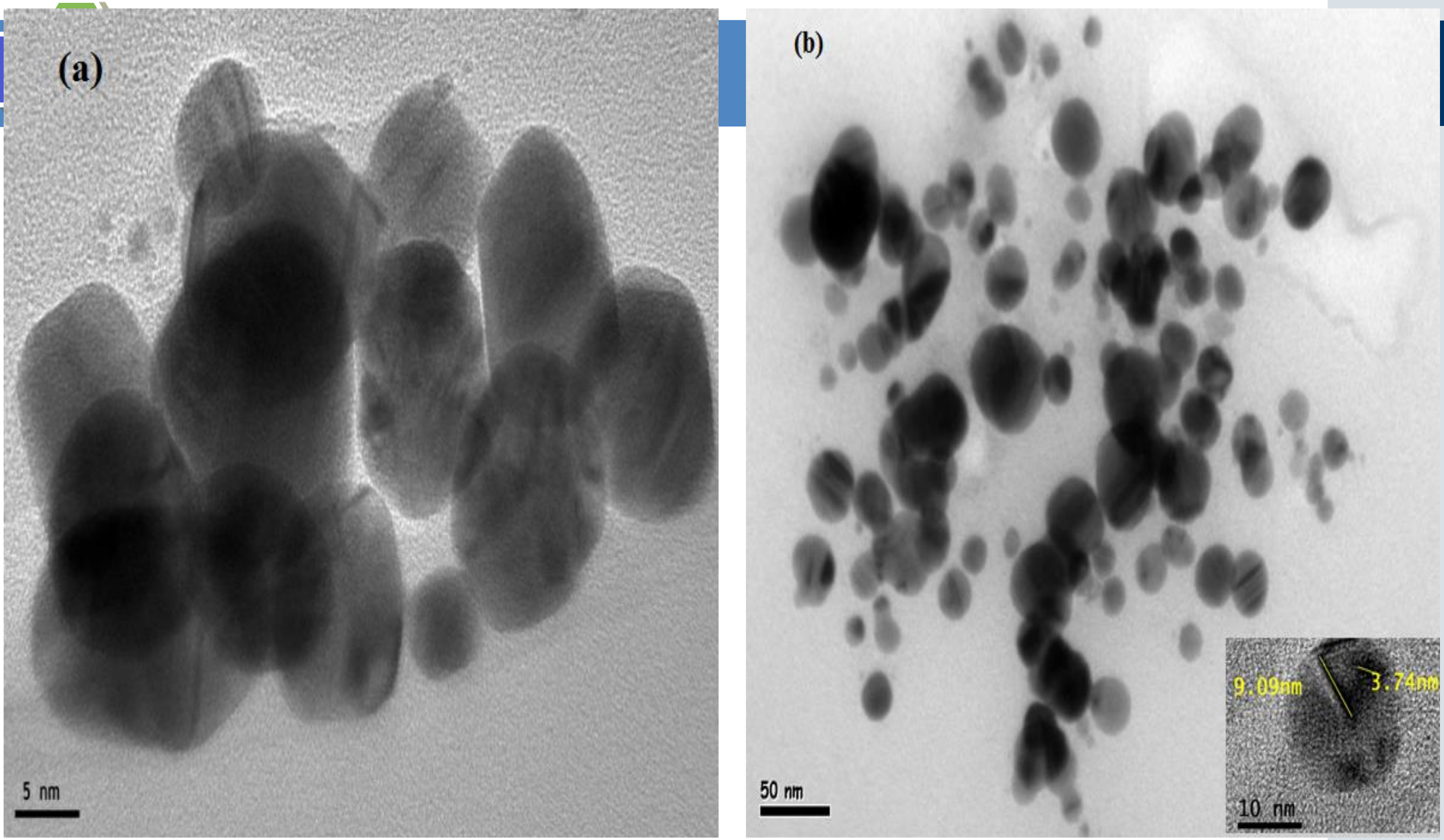


Figure 15: TEM micrographs of (a) Ag NPs and (b) silver AMPS/NIPAm hybrid polymer.

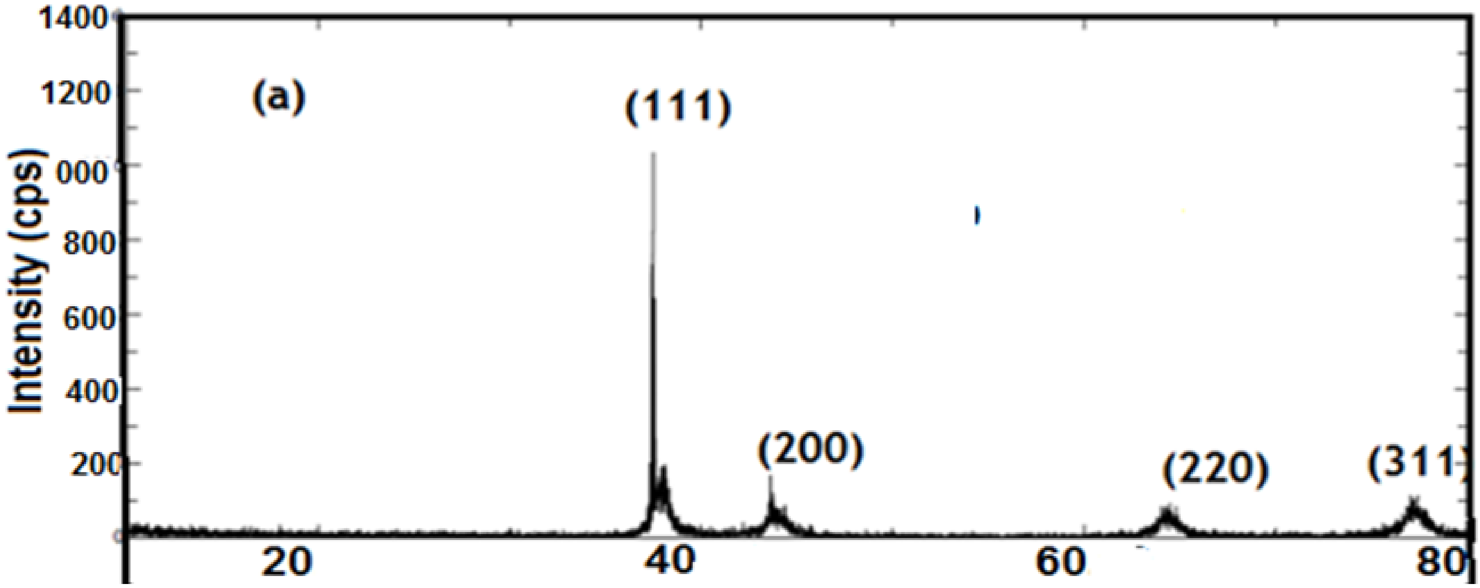


Figure 16: XRD patterns of (a) Ag NPs and (b) silver AMPS/NIPAm hybrid polymer.

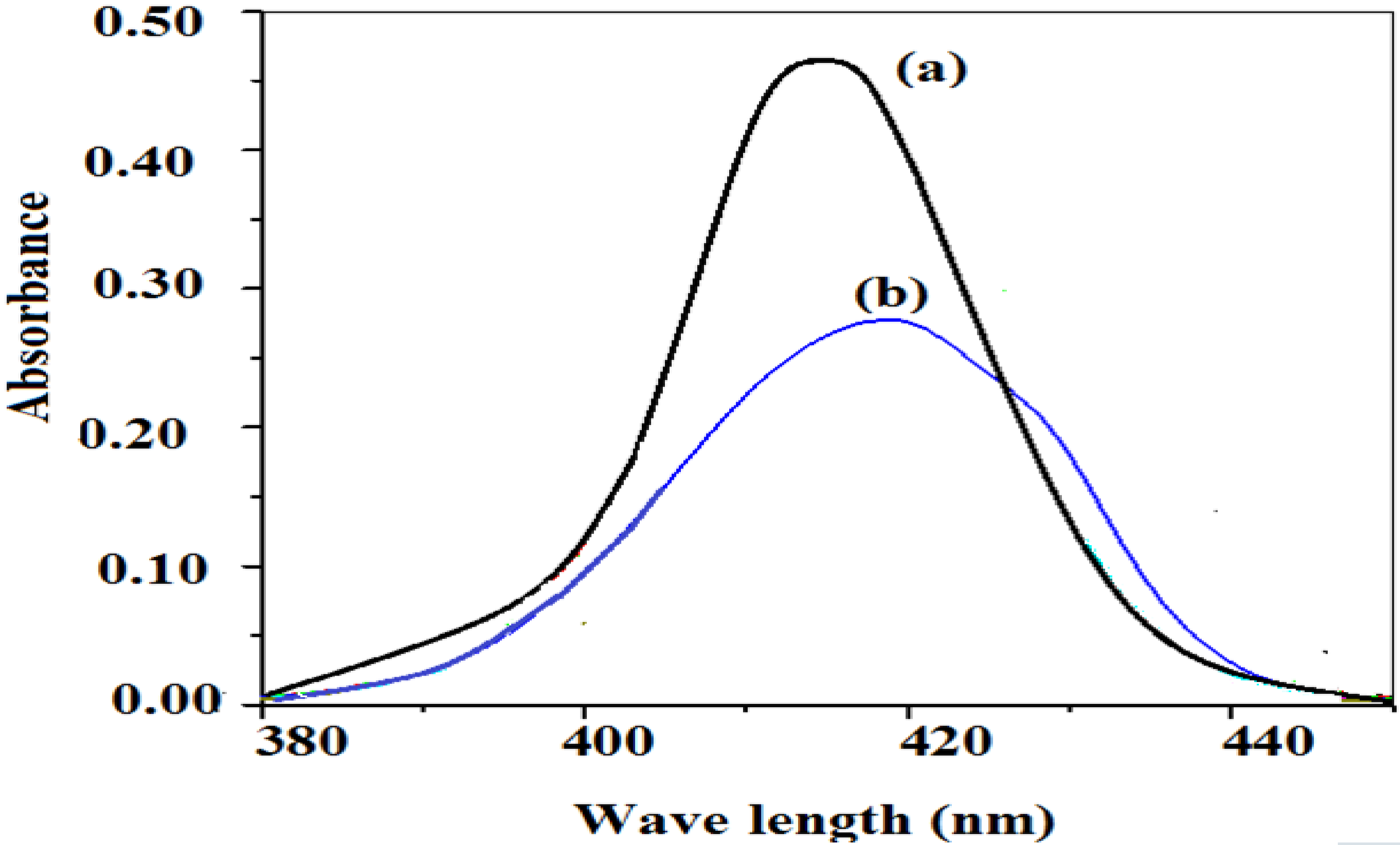


Figure 17.: UV-Vis absorption spectra of (a) Ag NPs coated with OA in hexane solution and (b) St/AMPS/NIPAm-Ag nanogel in aqueous solution

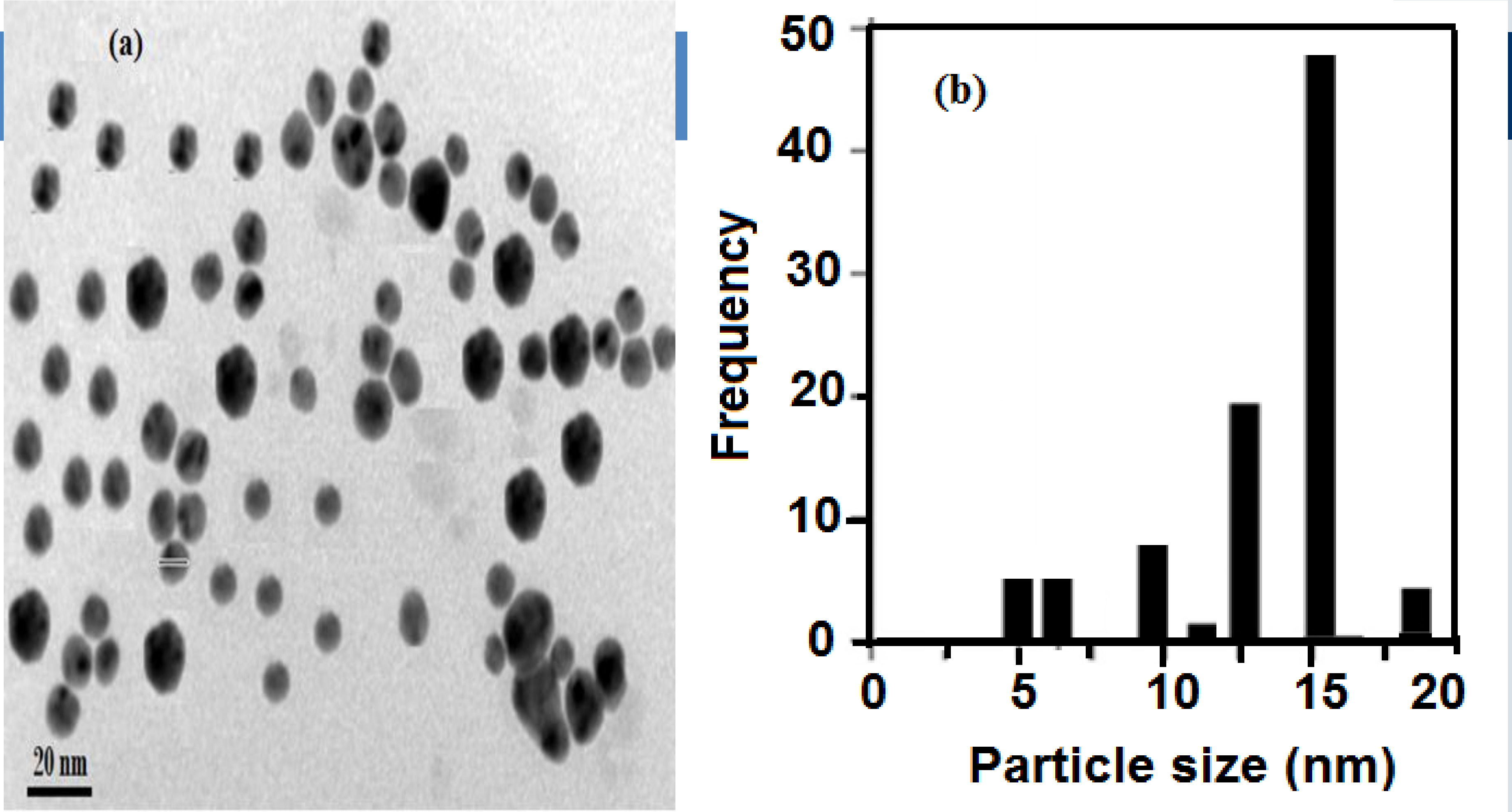


Figure 18: TEM micrographs of (a) St/AMPS/NIPAm-Ag nanogel and (b) its histogram.

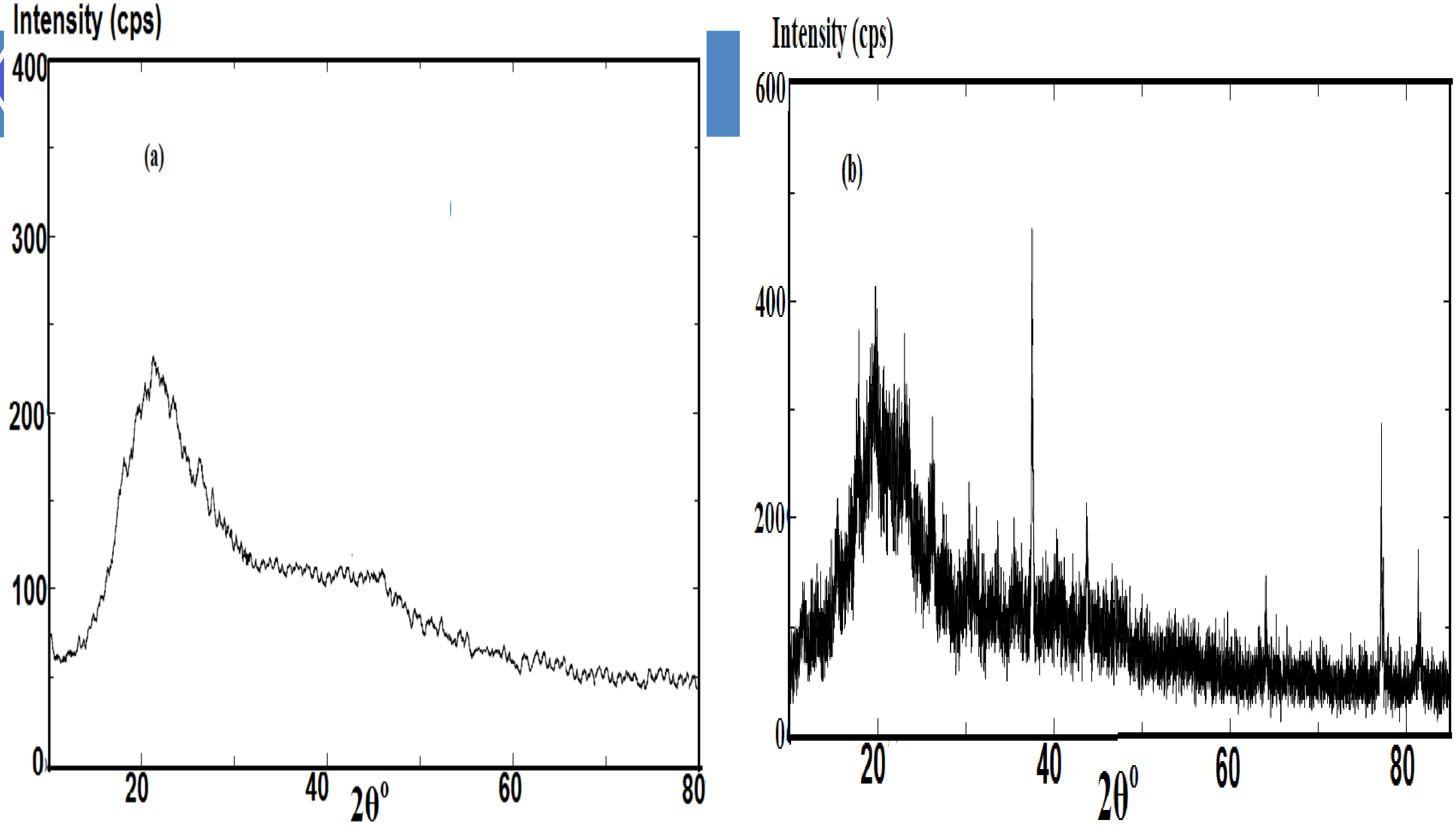
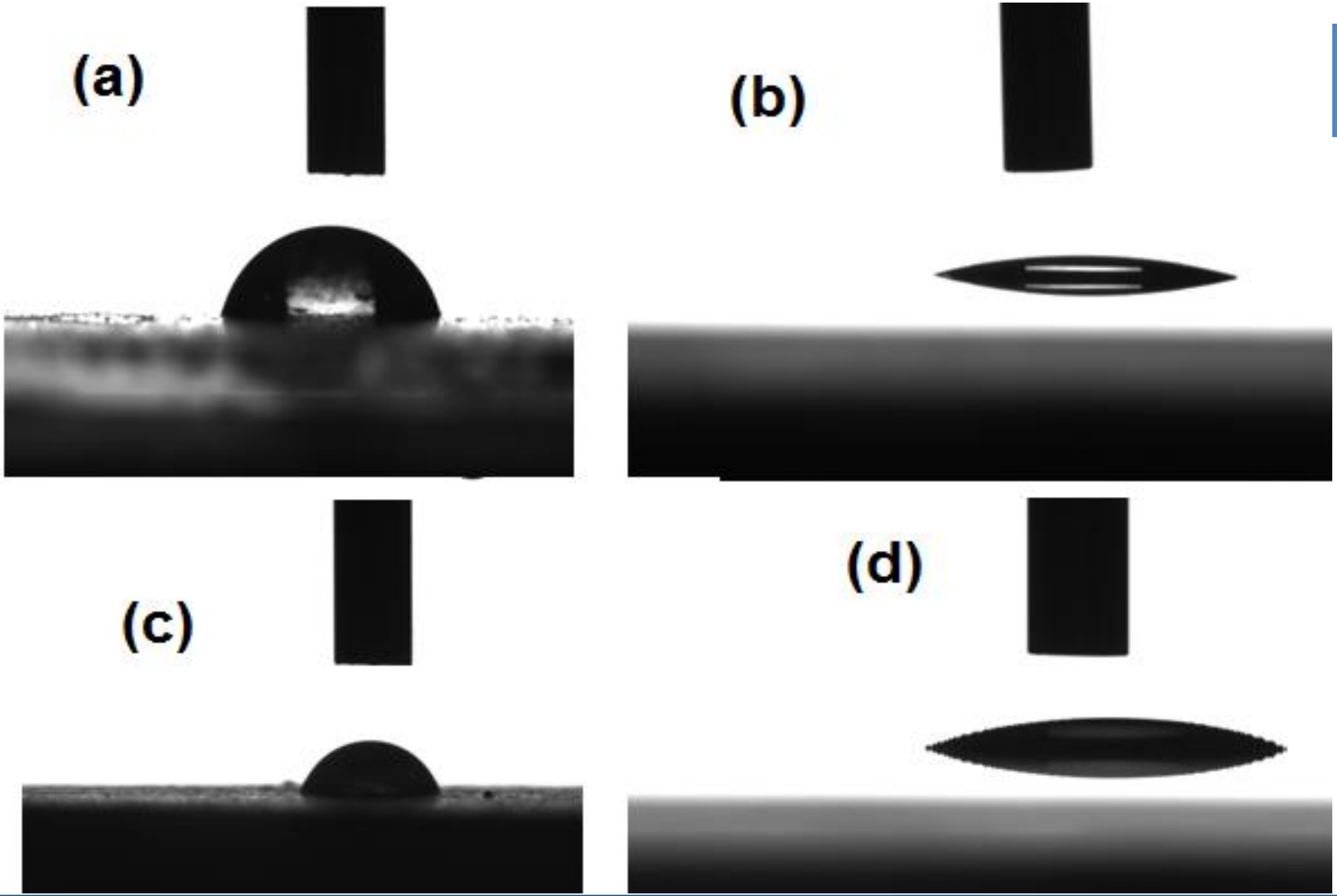


Figure 19: XRD pattern of (a) St/AMPS/NIPAm and (b) St/AMPS/NIPAm-Ag nanogel.



	Theta
a	67.5 °
b	12.3 °
c	85.1 °
d	26.1 °

Figure 20: Images of water droplet behavior on thin pellet of the silver nanoparticles surface: (**a**) AgNP capped with OA; (**b**) St/AMPS/NIPAm-Ag nanogel; (**c**) droplets of dispersed AgNP capped with OA; and (**d**) St/AMPS/NIPAm-Ag nanogel on glass.

Concentration (ppm)	Surface tension (γ) mN/m	Time to Reach Equilibrium (min)
500	41.2	2
250	42.5	5
100	53.4	15
10	62.5	25

Table 1: Surface tension characteristics and equilibrium time of the St/AMPS/NIPAm-Ag nanogels at 25 °C.

4. Application of A gNps

4.1 Acid stability of Ag NPs

- Silver is a noble metal with an inert chemical reactivity in its bulk form and is listed below hydrogen in the activity series of metals.
- Silver nanoparticles have high activity toward HCl and forming AgCl.
- The antimicrobial action of silver nano particle (AgNP) has led to apply it in medical which required stability to stomach fluid (pH 1.5).

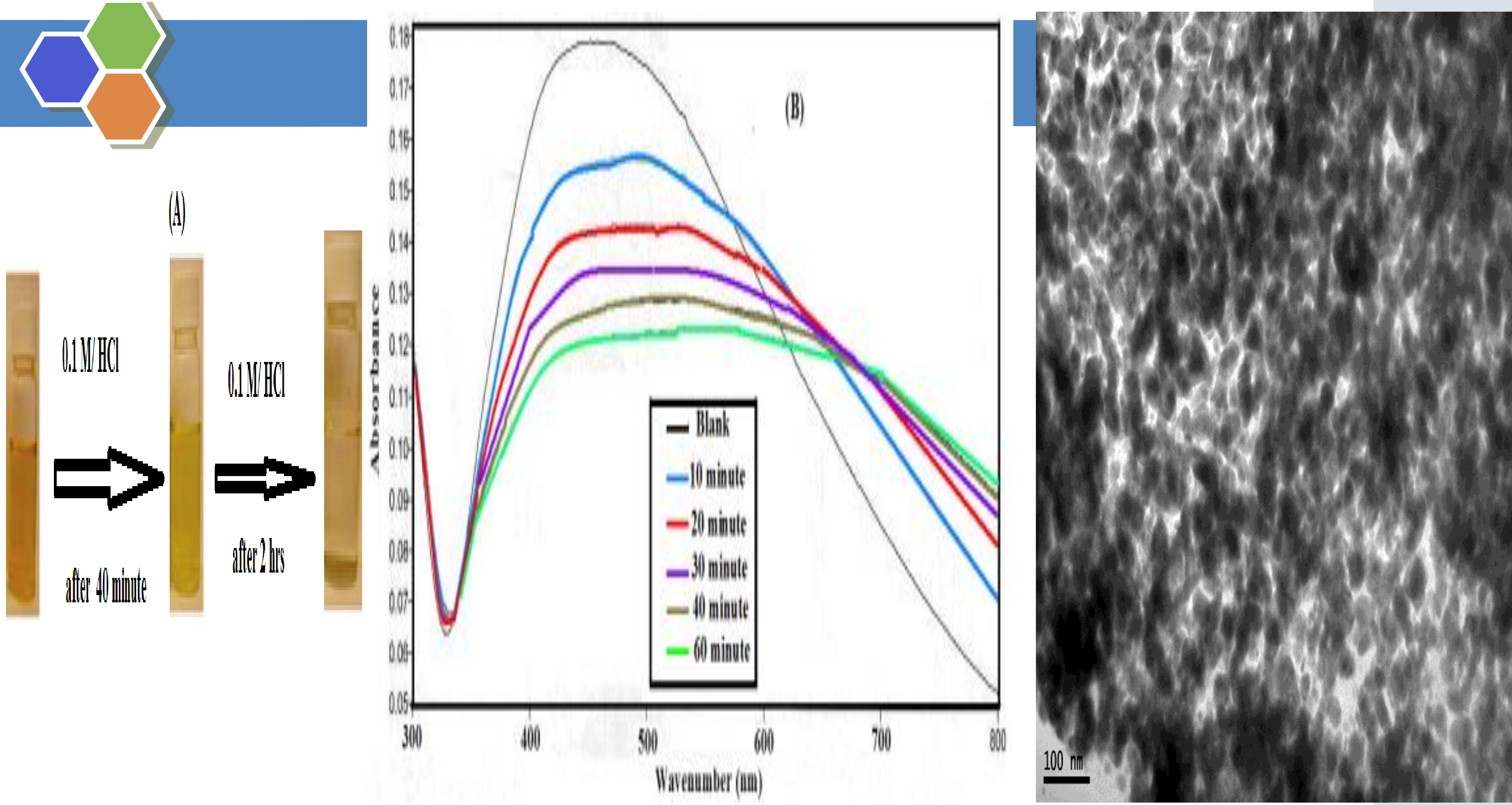


Figure 21: Citrate AgNPs a) digital photo b) UV-vis absorption spectra at interval times in 0.1 M HCl C) TEM of citrate AgNP after exposure to 0.1M HCl.

(A) (B) (C)

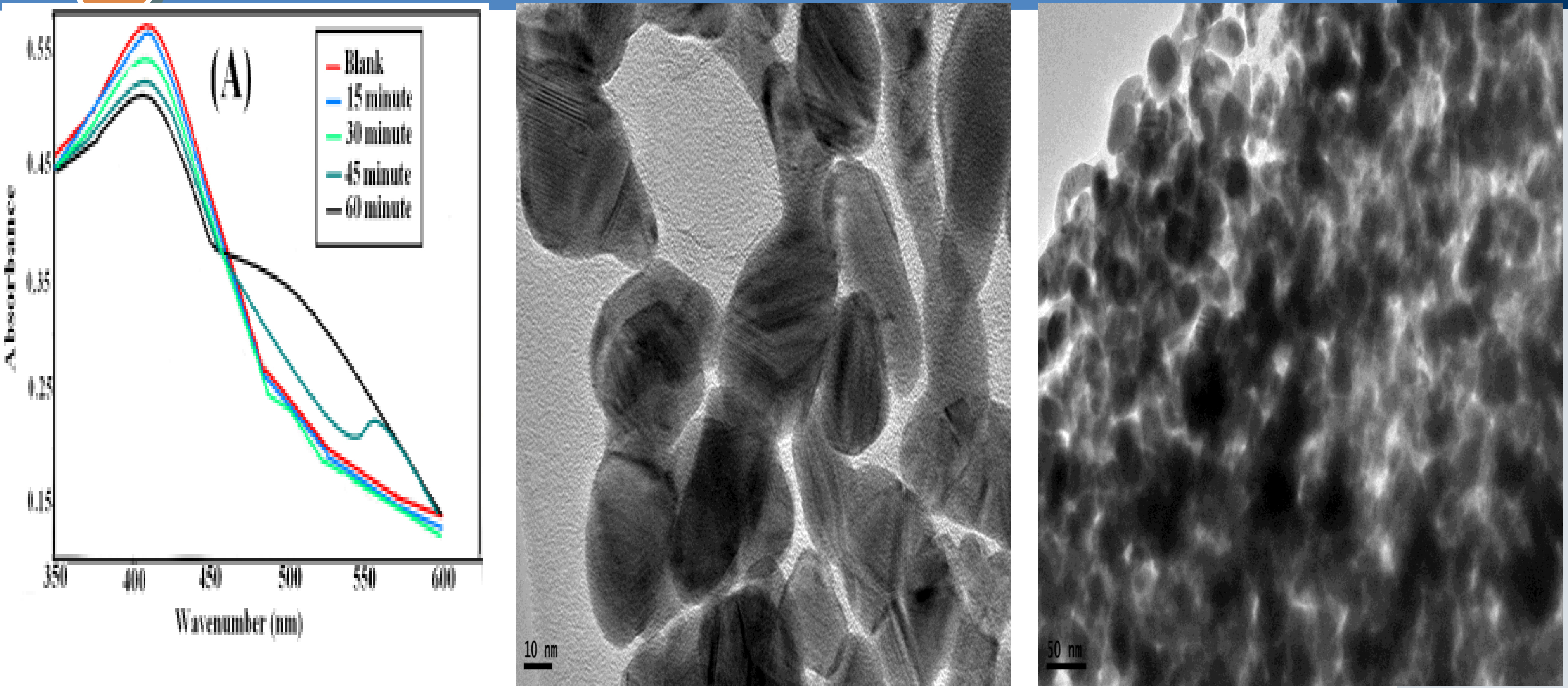


Figure 22: PVP/PEGSH AgNPs a) UV-vis absorption spectra at interval times in 0.5 M HCl, b) TEM after exposure to 10 hrs in 1M HCl and C) TEM exposure to 24 hrs in 1M HCl.

The effect of synthetic human stomach fluid (SSF) on Ag/PVA-SH nanoparticles stability.

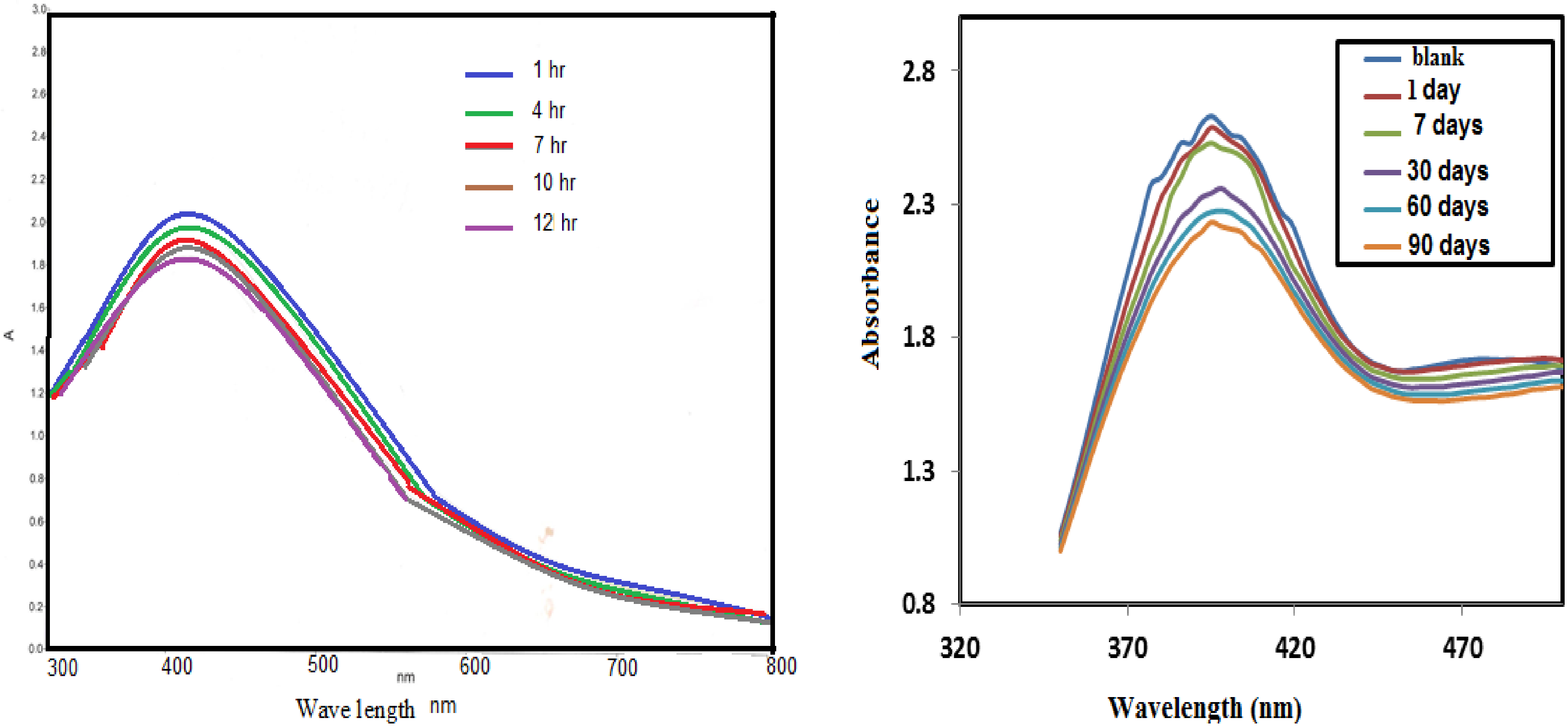
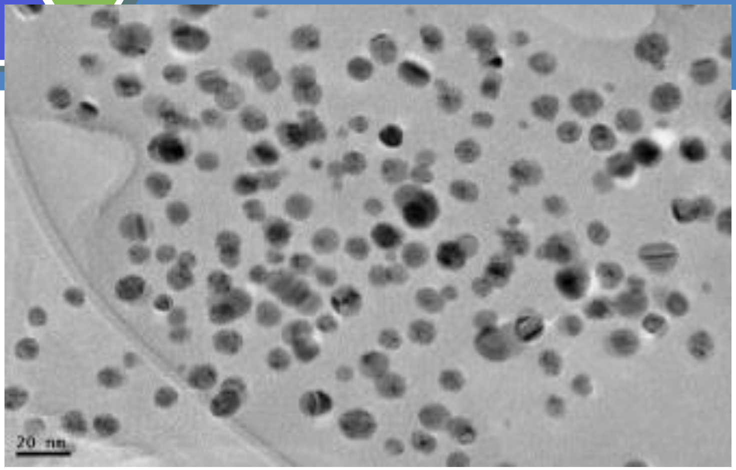


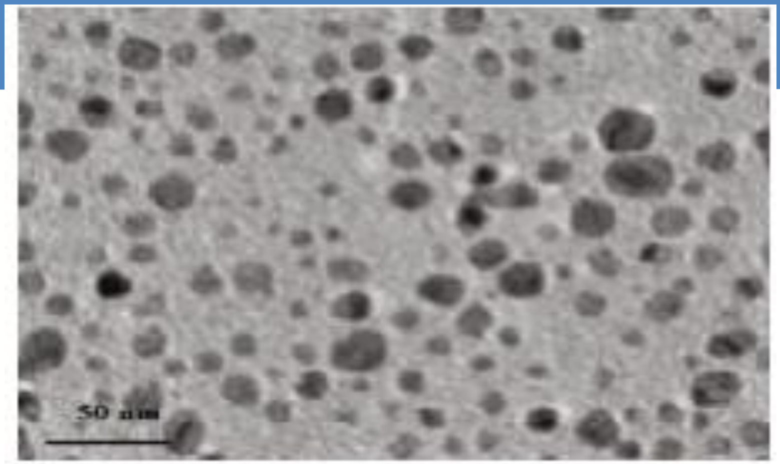
Figure 23: UV-vis absorption spectra of Ag/PVA-SH at interval times in a) SSF[1] (0.5 M) and b) 1 M HCl and 0.4 M glycine.

1. Kelly ME, Brauning SE, Schoof RA, Ruby MV. Assessing Oral Bioavailability of Metals in Soil. Columbus:Battelle Press,2002.

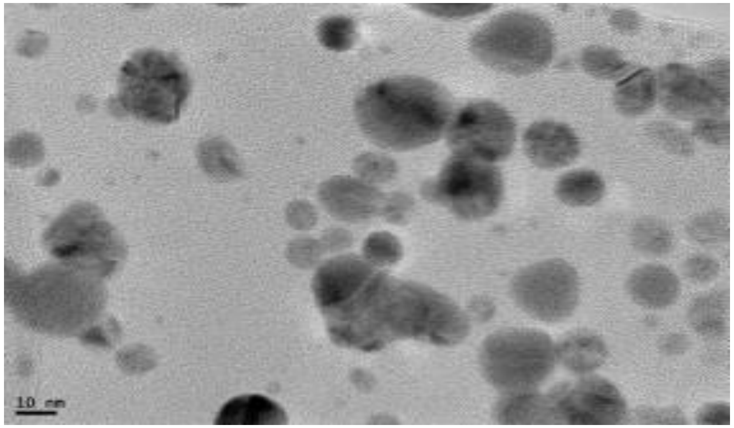
(a)



(b)



(c)



(d)

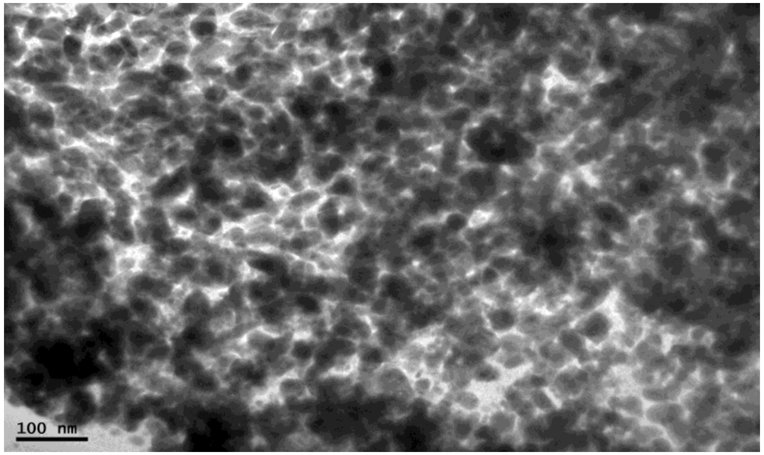


Figure 24: TEM image of Ag NP a) coated with PVA-SH, b) after exposure to 1M HCl for 1 week, c) after exposure to 1M HCl for 3 months and d) citrate Ag NP after exposure to 0.1M HCl for 1hr.

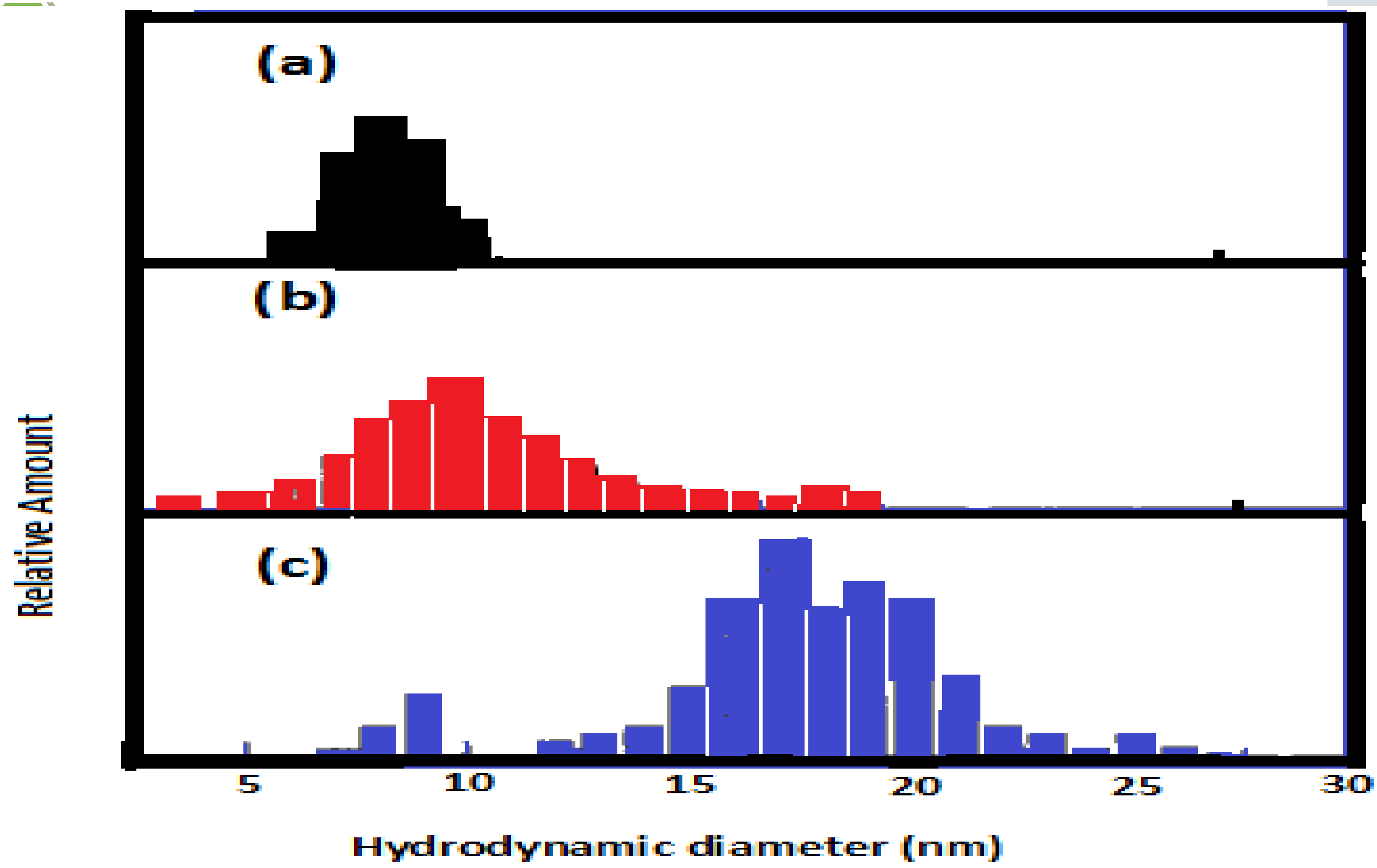
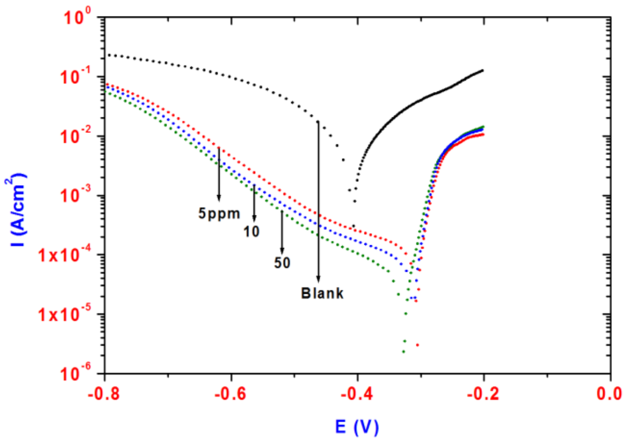
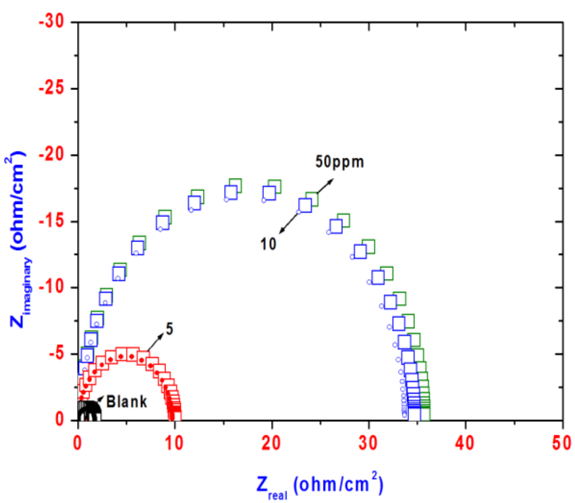


Figure 25.: Particle size distribution of Ag/PVA-SH in 1M HCl and 0.4 M of glycine at interval times a) 1hr, b) 24 hr and c) 7 days.





Polarization Method						EIS Method		
	Ba (mV)	Bc (mV)	E_{corr} (V)	i_{corr} mA/cm^2	IE%	R_p Ohm	Cdl (mF/cm^2)	IE%
Blank	69	120	-0.3955	839	______	1.80	334	_____
5ppm	50	394	-0.3061	152	81.8	10.1	137	82.1
10	41	173	-0.3139	49	94.1	35	106	94.8
50	46	195	-0.3282	44	94.7	36	104	95.0

Conclusion

- **This work reported as first time for highly dispersed and stabilized coated Ag NPs with method is simple, easy, cost effective and environment friendly.**

Highly dispersed silver coated nanoparticles were prepared using PEGSH and PVP/PEGSH and the results of TEM indicated that the particle size increases when using PVP/PEGSH and poly Polydispersity Indices decrease to give monodispersed particles and also the stability against HCl increases.

A novel method has been developed for the preparation of nanosilver, using Murrh as the reducing and stabilizing agents.

Silver nitrate was reduced to silver nanoparticles by p-chloroaniline in the presence of polyoxyethylene maleate 4-nonyl-2-propylene-phenol (NMA) as a stabilizer.

The produced AgNPs were used to prepare Ag/Amps/NIPAm hybrid nanogel.

A new developed method is used to prepare monodisperse hydrophobic silver nanoparticles using oleic acid and oleylamine by adding a trace amount of Fe^{3+} ions to increase the yield

Silver nanoparticles capped by oleic acid have been successfully used to prepare amphiphilic silver nanocomposite based on to St/AMPS/NIPAm- nanogel.

TEM and UV-vis spectroscoby indicated the high stability Ag/PVA-SH nanoparticles toward 1 M HCl and SSF for more than 90 days.

The interaction of lysozyme with Ag/PVA-SH nanoparticles was seen using various spectroscopic techniques. It was found that the quenching of lysozyme fluorescence by Ag-PVASH nanoparticles takes place with the complex formation between the protein and nanoparticle with 1:1 binding ratio. lysozyme gets partially unfolded in presence of Ag-PVSH nanoparticles.

The results of polarization measurements shows good protection of steel by eco friendly Ag-Murrh nanoparticles, Ag/AMPS/NIPAm nanocomposite and St./AMPS/NIPAm-Ag Amphiphilic Composite and all of them showed mixed type inhibitors.

Acknowledgement

Thank You!