SYNTHESIS, CHARACTERIZATION AND APPLICATION OF SILVER ALLIED NANOBIMETALLIC PARTICLES FOR CATALYSIS

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IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE AWARD OF DOCTOR OF PHILOSOPHY (Ph.D) DEGREE IN CHEMISTRY, IN THE DEPARTMENT OF CHEMISTRY, SCHOOL OF NATURAL & APPLIED SCIENCES, COLLEGE OF SCIENCE & TECHNOLOGY, COVENANT UNIVERSITY, OTA

MARCH, 2014

DECLARATION

I, **ADEKOYA, Joseph Adeyemi**, hereby declare that this thesis is a product of my own unaided research work. It has not been submitted, either wholly or in part to this or any other institution for the award of any degree, diploma or certificate. All sources of scholarly information that were used in this thesis were duly acknowledged.

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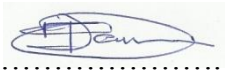
ADEKOYA, Joseph Adeyemi

CERTIFICATION

We certify that the thesis titled "Synthesis, Characterization and Application of Silver Allied Nanobimetallic Particles for Catalysis" is an original work carried out by Mr. Joseph Adeyemi Adekoya (CUGP07186) in the Department of Chemistry, Covenant University, Ota, Ogun state under the supervision of Dr. Enock O. Dare and Prof. M. Adediran Mesubi. We have examined and found the work acceptable for the award of a degree of Doctor of Philosophy in Chemistry.

Dr. Enock O. Dare — Signature/Date 
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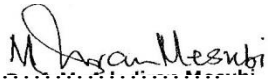
Prof. M. Adediran Mesubi — Signature/Date 
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DEDICATION

This thesis is dedicated to the Almighty God, my creator, provider and wisdom. To Him alone be all the glory.

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LIST OF ACRONYMS AND ABBREVIATIONS

EG	Ethylene glycol
DEG	Diethylene glycol
GLY	Glycerol
PET	Pentaerythritol
HDA	Hexadecylamine
TOPO	Trioctylphosphine oxide
DT	Dodecanethiol
DOE	Dioctyl ether
OA	Oleic acid
PVP	Polyvinylpyrrolidone
TEM	Transmission electron microscope
HRTEM	High resolution transmission electron microscope
XRD	X-ray diffractometer
p-XRD	Powder x-ray diffraction
EDX	Energy dispersive x-ray microanalyzer
XPS	X-ray photoelectron spectrometer
AES	Auger electron spectroscopy
UV-Vis	Ultraviolet-Visible
PL	Photoluminescence
PLE	Photoluminescence excitation
SC	Trisodium citrate trihydrate
NPs	Nanoparticles
BNPs	Bimetallic nanoparticles
4-NP	4-nitrophenol
p-NP	para-nirophenol
fcc	Face centered cubic
hcp	Hexagonal close packed
1D	One dimension
2D	Two dimensions
3D	Three dimensions
EXAFS	Extended X-ray absorption fine structure
SPR	Surface plasmon resonance

SRB	Surface resonance band
CVD	Chemical vapour deposition
PVD	Physical vapour deposition
MBE	Molecular beam epitaxy
MOCVD	Metallorganic chemical vapour deposition
STP	Standard temperature and pressure
CTAB	Cetyltrimethylammonium bromide
SDS	Sodium dodecyl sulphate
AOT	Dioctyl sulfosuccinate sodium salt
IR	Infra-red
FWHM	Full width at half maximum
LO	Lattice Oxygen
eV	Electron volt
nm	Nanometer
Å	Angstrom
^{0}C	Degree Celsius
K	Kelvin
aq	Aqueous

ABSTRACT

The synthesis of seed mediated AgM (M = Co, Ni, Ru, Pd and Pt) allied nanobimetallic particles was successfully carried out by simultaneous reduction in aqueous and non-aqueous solutions. The formation of novel monodispersed and unaggregated bimetallic nanoparticles capped by polymer and organic chelating agents was desirable for catalysis and photonic applications. As a result, wet chemical approach was successfully deployed to produce some novel bimetallic silver allied nanoparticles distinct in morphology from their monometal analogues. Optical and morphological investigation of the nanoparticles revealed that the shape, size and size distribution of the silver allied nanoparticles depended on the stabilizer or capping agent, mole ratio of inorganic sources, temperature and time of reaction. The analyses of the nanoparticles also showed that formation of uniformly distributed, highly crystalline and monodispersed/polydispersed silver allied bimetallic nanocomposites of different dimensions within the quantum realm had been achieved. Consequently, the alloy or core-shell crystalline structure of nanocomposites was also established. Furthermore, X-ray photoelectron spectrometer (XPS) scan established the surface elemental composition and the binding energy of the nanocomposites. As a result, a new morphology described as hybrid quasi nanocubes entangled in nanowebs was discovered for polyvinylpyrrolidone (PVP) stabilized AgPt nanoparticles passivated by diethylene glycol (DEG) and ethylene glycol (EG) which evolved a core-shell structure. The mean size of the nanocubes was 30.45 ± 6.23 nm, while XRD analysis strongly suggested that the nanocubes pertained to {111} plane of face-centered cubic Ag. Meanwhile, the nanoweb was formed as a result of phase contraction by Pt. Likewise, electron micrographs of Ag/Ru nanoparticles capped by dodecanethiol/polyol at 200°C; 3h showed the presence of novel well-ordered core-shell structures with particle size in the range of 8.2 ± 0.7-11.4 ±1.3 nm. In addition, novel core-shell nanoparticles of AgPt capped by hexadecylamine (HDA) were discovered from their electron micrographs. The X-ray diffraction spectra suggested dominance of face-centered cubic structure with 2θ reflections slightly shifted from silver peaks. This is reminiscent of noble metals forming alloy or core-shell morphology with silver. Similarly, AgCo and AgNi nanoparticles passivated by polyol particularly revealed the formation of nearly uniform, monodispersed core-shell structure which proved to be optically active by characteristic surface plasmon resonance band blue shifted for pentaerythritol (PET) and trisodium citrate trihydrate (SC) derived nanoparticles. Further optical characterization also revealed the fluorescent potential of AgCo, AgNi, AgPt, AgPd and AgRu sols as a result of their S_1-S_0

vibrational mode relaxation with appreciable emission of appropriate quantum yield. Finally, the catalytic potential of the nanocomposites investigated using 4-nitrophenol in the presence of sodium borohydride at 299 K indicated a pseudo-first-order kinetics which gave $AgPd/PVP_{GLY}$ a rate constant of 5.4×10^{-3} s^{-1}. This value is significantly higher than 2.8×10^{-3} s^{-1} reported for poly(ethylenimine)-stabilized Ag nanoparticles (Ag-HNP), but relatively lower than $9.2 \pm 1.7 \times 10^{-3}$ s^{-1} recorded for AuAg-HNP due to the fact that Au/Ag bimetallic nanoparticles have been shown to exhibit greater quantum size effect. These results strongly indicate the application of these materials for catalysis and optoelectronics.