shows peaks of $Ru_{3p3/2}$, Ag_{3d}, N_{1s}, Cl_{2p} (respectively at the binding energy (BE) values of 461.5, 367.2, 399.2, and 197.1 eV) and elemental molar ratios respectively equal to 1.0:1.07:7.63:2.10, that fit with the experimental elemental analysis. TGA measurements show a weight loss of about 33% in the range 130–270 °C due to the loss of three pyrazine molecules, followed by a two-step demolition (range 270–600 °C) leading to the metals (ca. 32%). An XRPD spectrum of the massive product **4** was found to be identical to a simulated profile achieved from the single-crystal structure. Red crystals were obtained by slow diffusion of a solution of $AgNO_3$ in MeCN (3.5 mL, 7.1×10^{-3} M) into a brown solution of $[RuCl_2(pyz)_4]$ in TCE (3 mL, 1.9×10^{-3} M), by using pure MeCN (1.5 mL) as a spacer between the two solutions.

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Synthesis of Metal Nanoparticles by Using Polyoxometalates as Photocatalysts and Stabilizers[**]

Aristidis Troupis,[*] Anastasia Hiskia, and
Elias Papaconstantinou[*]

Formation of colloidal metal nanoparticles is a topic of great interest from a fundamental and practical point of view.[1–4] Metal nanoparticles have been obtained by thermal,[3, 5] photochemical,[6] radiolytic,[7] electrochemical,[8] or sonochemical methods,[9] by using various reagents.

Polyoxometalates (POMs) are well-defined metal–oxygen cluster anions.[10, 11] Their redox chemistry is characterized by

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[*] A. Troupis, Dr. E. Papaconstantinou, Dr. A. Hiskia
Institute of Physical Chemistry
NCSR Demokritos
153 10 Athens (Greece)
Fax: (+30)16511766
E-mail: atroup@chem.demokritos.gr, epapac@mail.demokritos.gr

A. Troupis
Chemical Engineering Department
National Technical University
157 80 Athens (Greece)

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their ability to undergo stepwise, multielectron redox reactions, whilst their structure remains intact. They participate in catalytic redox processes as electron relays. POMs can be reduced in a plethora of ways, for example, photochemically,[12] through ^{60}Co–γ-radiolysis,[13] electrolytically,[10] and with reducing reagents[14] [Eq. (1) S = substrate]. Various oxidants, which include O_2 and H_2O_2, restore reduced POM to the original form, which completes the photocatalytic cycle. Gordeev noticed the ability of radiolytically two-electron-reduced 12-tungstophosphate, $[PW_{12}O_{40}]^{5-}$, to reduce Ag^+ ions into stable silver hydrosols.[15]

$$\mathrm{POM} + \mathrm{S} \rightarrow \mathrm{POM(e^-)} + \mathrm{S_{ox}} \quad (1)$$

We have shown[16] that illumination of a deaerated POM/S/M^{n+} solution (POM: $[PW_{12}O_{40}]^{3-}$, $[SiW_{12}O_{40}]^{4-}$; S: propan-2-ol or 2,4-dichlorophenol; M^{n+}: Ag^+, Pd^{2+}, Cu^{2+}) with an ionic strength of 0.1 M, results in formation of large metal particulates (easily retained by a 0.45 μm filter) which rapidly precipitate out. This route has been proposed as a potential process for the removal–recovery of valuable or toxic metals.

We present here a low ionic strength (no addition of $HClO_4$ and $NaClO_4$) photolysis method with near-visible and UV light, which leads to the formation of metal nanoparticles, through a process in which POMs serve both as photocatalysts, reducing reagents, and stabilizers. Specifically, several metal ions (Ag^+, Pd^{2+}, Au^{III}, and Pt^{IV}) can form metal nanoparticles in the presence of photochemically reduced POMs, in aqueous solutions, according to Equation (2); M_{coll} = colloidal metal. This reaction takes place at ambient temperature, within a few seconds, and without the addition of any stabilizer. The diversified redox chemistry of POM and the potential that the reactions in Equations (1) and (2) may be separated in time and space, or occur in a one-pot system, makes these compounds capable of acting as new multifunctional mediators, which show both reducing and stabilizing ability, in the synthesis of metal nanoparticles.

$$\mathrm{POM(e^-)} + \mathrm{M}^{n+} \rightarrow \mathrm{POM} + \mathrm{M^0}_{\mathrm{coll}} \quad (2)$$

A typical experiment in which Equations (1) and (2) proceed separately is presented below. A representative Keggin-structure POM, $[SiW_{12}O_{40}]^{4-}$, was chosen to study the reaction in Equation (2), between the one-equivalent of the photochemically reduced tungstosilicate, $[SiW_{12}O_{40}]^{5-}$, and the metal ions. The $[SiW_{12}O_{40}]^{5-}$ ion was obtained by photolysis of a deaerated propan-2-ol/$[SiW_{12}O_{40}]^{4-}$ aqueous solution with λ > 320 nm light, in the presence of, for instance, propan-2-ol as a sacrificial reagent[12] [Eq. (3)].[12c]

$$2\,[\mathrm{SiW_{12}O_{40}}]^{4-} + (\mathrm{CH_3})_2\mathrm{CHOH} \xrightarrow{h\nu} 2\,[\mathrm{SiW_{12}O_{40}}]^{5-} + (\mathrm{CH_3})_2\mathrm{C{=}O} + 2\,\mathrm{H^+} \quad (3)$$

The photoreduction of 12-tungstosilicate was monitored at 730 nm, the characteristic absorption of the one-electron-reduced, blue POM, $[SiW_{12}O_{40}]^{5-}$ (Figure 1). After irradiation ceased, Ag^+, Pd^{2+}, $PtCl_6^{2-}$ (0.1 mM), or $AuCl_4^-$ (1 mM) ions were added to the photolysed solution. Within a few seconds the absorption at 730 nm disappeared and the solution turned gradually yellow (Ag), pink (Au), or black-brown (Pd, Pt), [Eq. (4)]. The spectra obtained after 2 minutes, assigned to plasmon-resonance absorbance of the corresponding metal nanoparticles, are shown in Figure 1.[17]

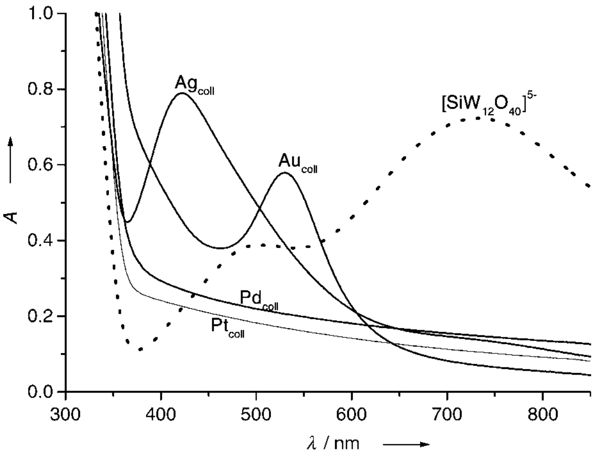

Figure 1. Absorption spectra of metal nanoparticles (Ag, Au, Pd, Pt) in solution, obtained after thermal reaction of photogenerated 1-equivalent-reduced POM, $[SiW_{12}O_{40}]^{5-}$ (about 0.35 mM; spectrum shown), with the corresponding metal ions (Ag^+, Pd^{2+}, $[PtCl_6]^{2-}$ (0.1 mM) or $[AuCl_4]^-$ (1 mM)); pH 5. coll = colloidal.

$$n\,[\mathrm{SiW_{12}O_{40}}]^{5-} + \mathrm{M}^{n+} \rightarrow n\,[\mathrm{SiW_{12}O_{40}}]^{4-} + \mathrm{M^0} \quad (4)$$

Thus, the reaction in Equation (2) proceeds at room temperature within seconds and utilizing a mild reductant, $[SiW_{12}O_{40}]^{5-}$, whereas other reductive methods that proceed promptly at room temperature use rather strong reductants such as BH_4^-, hydrogen atoms, or organic radicals, produced upon radiolysis or sonolysis of aqueous solutions. On the other hand, conventional processes that use mild reducing agents often need heat to enable them to proceed within minutes or days.[5]

Step 2 functions because of: a) the ability of reduced POM to transfer the electrons efficiently to many reagents[14] and b) the lower potential of the one-equivalent-reduced tungstate couple $[SiW_{12}O_{40}]^{4-}/[SiW_{12}O_{40}]^{5-}$ (0.057 V vs. NHE; NHE = normal hydrogen electrode) relative to Ag^+/Ag^0 (0.799 V vs. NHE), $AuCl_4^-/Au^0$ (0.99 V vs. NHE), Pd^{2+}/Pd^0 (0.987 V vs. NHE), or $PtCl_6^{2-}/Pt^0$ (0.725 V vs. NHE).

The TEM pattern of the metal particles indicated in Figures 2–5 verify the formation of metal nanoparticles in the process. The Au (Figure 2) or Ag (Figure 3) particles produced are almost spherical with a diameter of 13.1 ± 3.9 nm (±30%, sample population 197) and 15.3 ± 3.4 nm (±22%, sample population 177), respectively. The palladium particles (Figure 4) obtained were of 5.0 ± 1.1 nm (±22%, sample population 97). In the case of platinum (Figure 5), smaller particles of 2.7 ± 0.6 nm diameter (±24%, sample population 98) were assembled to give larger spheres with an average diameter of 24.0 ± 7.2 nm (±30%). The colloids obtained were stable against aggregation for over two months.

The restriction of the size of the metal particles to the nanometer scale is attributed to the stabilizing role of POM

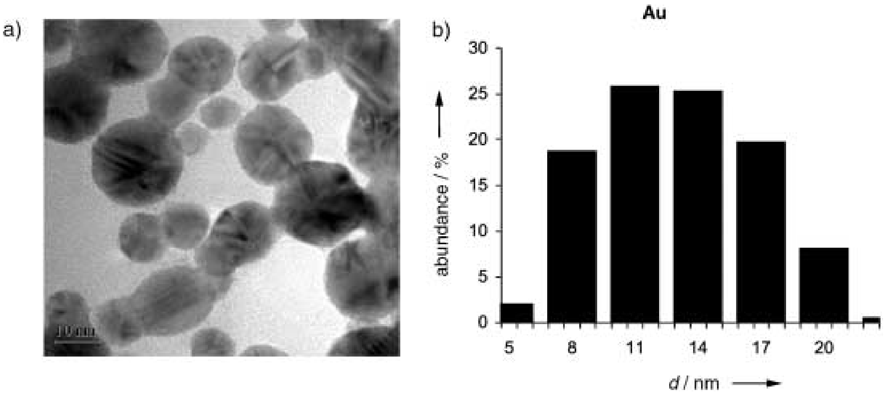

Figure 2. a) Transmission electron micrograph and b) size histogram of the Au particles.

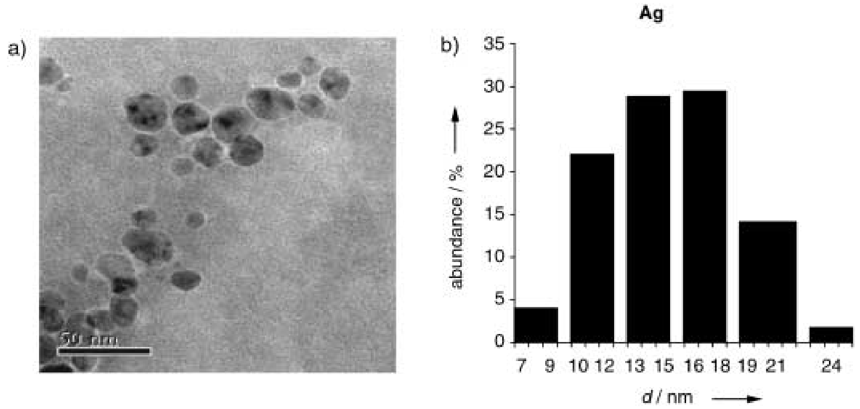

Figure 3. a) Transmission electron micrograph and b) size histogram of the Ag particles.

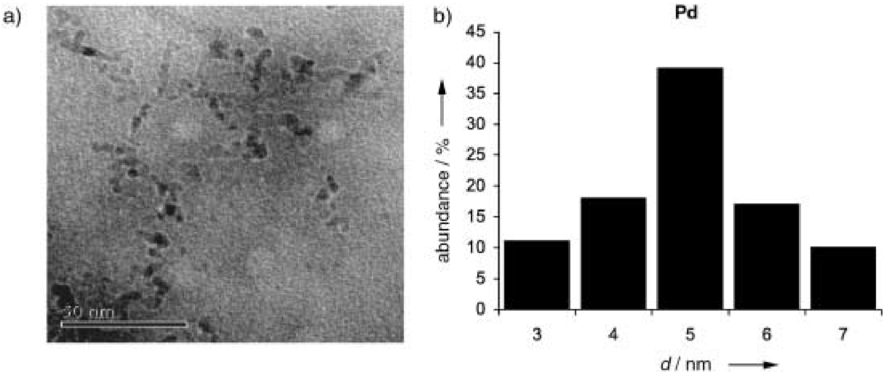

Figure 4. a) Transmission electron micrograph and b) size histogram of the Pd particles.

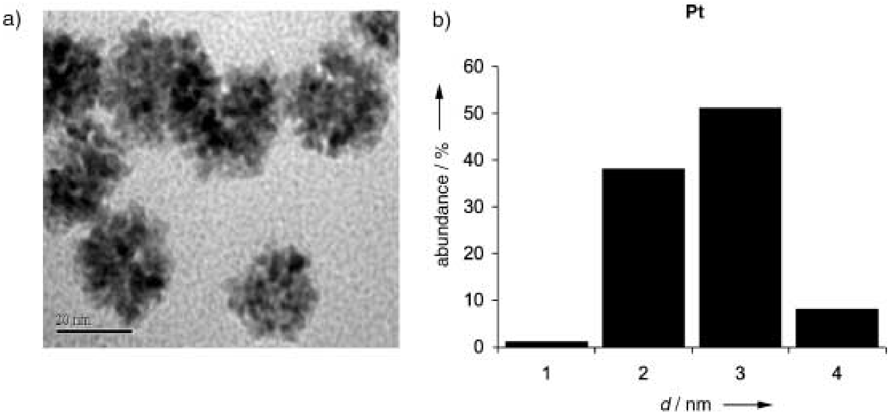

Figure 5. a) Transmission electron micrograph and b) size histogram of the Pt particles.

because: a) the colloidal solution contains no other potential stabilizing reagent but POM, b) the volume of 12-tungstosilicate (considered to be spherical, with a diameter of about 12 Å) and its (4 –) negative charge (the anion is not protonated, even at pH 1[18]) could account for the prevention of agglomeration of the metal particles, as for other POM,[3c] c) the stabilizing role of POM in organic systems (acetone or acetonitrile solutions) has been reported in a process in which H_2 was the reducing agent for Ir or Rh complexes, while the POM $[Bu_4N]_9[P_2W_{15}Nb_3O_{62}]$ functioned solely as a stabilizer. In addition, TEM, ion-exchange, and electrophoresis experiments revealed that POMs attach to the surface of Ir^0 or Rh^0 nanoclusters,[3] and d) the ability of $[SiW_{12}O_{40}]^{4-}$ not only to attach but also to self-assemble onto Ag(111) or Au(111) surfaces has been demonstrated.[19] Addition of $NaClO_4$ 0.1 M into the colloidal solutions leads to immediate precipitation in all cases.

These results have been obtained through the separation of the photochemical reaction from the thermal reaction. However, combination of both in a one-pot system gave satisfactory results with Ag^+ ions. Figure 6 shows the gradual development of the yellow color (410 nm), characteristic of silver-nanoparticle absorbance, upon photolysis of a deaerated $[SiW_{12}O_{40}]^{4-}$/propan-2-ol/Ag^+ aqueous solution. It is noteable that, in all experiments, the POMs remained intact in the process, determined from the stability of the absorbance peak at 263 nm (Figure 6), which is characteristic of the oxidized form of Keggin-structured POMs.

In summary, a novel and facile method has been proposed to synthesize metal nanoparticles directly from aqueous solutions, by use of POMs to serve as reducing reagents, photocatalysts, and stabilizers. As the solubility of POMs can be tuned by altering the counterion, which renders these compounds soluble in many organic solvents without affecting their redox properties, the process could be extended to nonpolar solvents. This prospect is attractive as the solubility of the reducing agent and the stabilizer are limiting factors in the chemical-reductive synthesis of metal nanoparticles.[5]

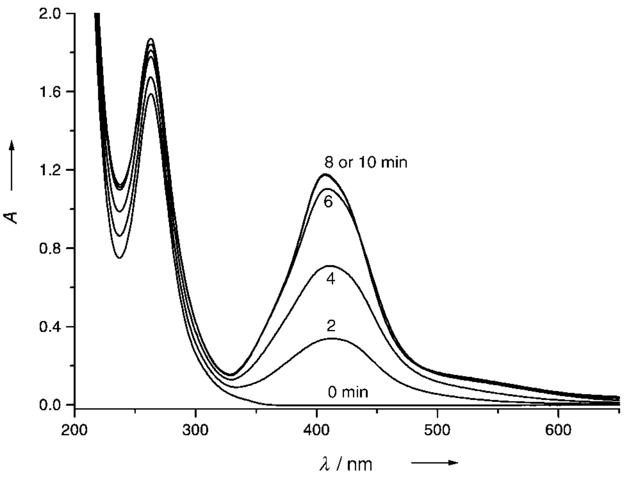

Figure 6. Photolysis profile: the formation of colloidal silver at different illumination times ($\lambda \approx 410$ nm) and the stability of $[SiW_{12}O_{40}]^{4-}$ photocatalyst ($\lambda = 263$ nm). Photolysis of a deaerated solution containing propan-2-ol (0.5 M), $[SiW_{12}O_{40}]^{4-}$ (0.035 mM), Ag^+ (0.1 mM) at pH 5 ($\lambda >$ 320 nm).

Experimental Section

$K_4[SiW_{12}O_{40}]$ was synthesized according to literature methods.[18] The metal ions added to the photolysed solution were aqueous solutions of $AgNO_3$, $PdCl_2$, $HAuCl_4$, or H_2PtCl_6.

In photolysis experiments, an aqueous solution of $SiW_{12}O_{40}^{4-}$ 0.7 mM and propan-2-ol 0.5 M, at pH 5, was put into a spectrophotometer cell (1 cm path length) deaerated with Ar and covered with a cerum cap. Photolysis was performed with a 1000 W Xe arc lamp, the light intensity of which was mechanically reduced by approximately 40%, while cut-off filters (up to 320 nm) were used to avoid direct photolysis of organic substrates. The absorption spectra of metal particles or catalyst were taken with a UV/Vis/NIR Spectrometer (Perkin Elmer Lambda 19), and the degree of reduction of POM in photolyzed, deaerated solutions was calculated from the known extinction coefficient of reduced catalyst, $SiW_{12}O_{40}^{5-}$, at 730 nm ($0.21 \times 10^4\,M^{-1}cm^{-1}$). TEM images were obtained using a Philips 200 kV microscope, and the samples were prepared by placing microdrops of colloid solution on a Formvar/carbon coated copper grid.

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Light-Controlled Nitric Oxide Generation from a Novel Self-Assembled Monolayer on a Gold Surface**

Salvatore Sortino,* Salvatore Petralia,
Giuseppe Compagnini, Sabrina Conoci, and
Giuseppe Condorelli

Increasing evidence demonstrates that nitric oxide (NO) plays important roles in numerous physiological processes.[1–8] For instance, it is involved in the bioregulation of functions such as vasodilatation, neurotransmission, and hormone secretion in living bodies. In addition to these effects, NO has also been reported to act as efficient anticancer agent that inhibits key metabolic pathways to block the growth of or to kill cells.[9–13] This has stimulated intense interest in com-

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[*] Dr. S. Sortino, Dr. S. Petralia, Prof. G. Condorelli
Dipartimento di Scienze Chimiche
Università di Catania
Viale Andrea Doria 8, 95125 Catania (Italy)
Fax: (+39)095-580-138
E-mail: ssortino@mbox.unict.it

Dr. G. Compagnini
Dipartimento di Scienze Chimiche
Università di Catania
and
Istituto Nazionale per la Fisica della Materia
Unità di Catania (Italy)

Dr. S. Conoci
Si optoelectronics, bio- and nano-systems Corporate Technology R&D, ST Microelectronics Stradale Primosole 50,
95125 Catania (Italy)

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