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Synthesized copper nanoparticles by sonoelectrodeposition for gas filter applications

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Abstract

Copper nanoparticles (CuNPs) were prepared with different diameters by sonoelectrodeposition technique using Electrodeposition process coupled with high-power ultrasound horn (Sonoelectrodeposition). The particle diameter of the CuNPs was adjusted by varying $CuSO_4$ solution acidity (pH) and current density. The morphology and structure of the CuNPs were examined by X-ray diffraction (XRD) and Scanning Electron Microscopy (SEM). It was found that the size of the produced copper nanoparticles ranged between 22 to 77 nm, where the diameter of CuNPs increases with reduction the solution acidity from 0.5 to 1.5 pH and increasing the current density of the deposition from 100 to 400 nm. Finally the produced CuNPs were pressed to fabricate disc filter and then the permeability, porosity, and filtration efficiency were determined which showed good efficiency.

Key words

Sonoelectrodeposition, copper nanoparticles, nano filter.

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تصنيع جسيمات النحاس النانوية بطريقة الترسيب بالموجات الفوق الصوتية لتطبيقات مرشحات الغاز

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الخلاصة

تم تحضير الجسيمات النانوية النحاسية (CuNPs) بأقطار مختلفة بواسطة تقنية الموجات فوق الصوتية كمصدر إضافي للطاقة لدعم التحضير الكهروكيميائي (Sonoelectrodeposition)، حيث تم تسليط نبضات للتيار الكهربائي والموجات فوق الصوتية. أجري فحص قطر الجسيمات عن طريق تغيير حامضية المحلول (pH) وكثافة التيار. أجريت فحوصات مورفولوجيا وبنية الدقائق النانوية النحاسية بواسطة حيود الأشعة السينية (XRD) المجهر الإلكتروني الماسح الضوئي (SEM). وجد ان حجم دقائق النحاس المنتجة تتراوح بين 22 الى 77 نانومتر حيث يزداد قطر الدقائق بنقصان حامضية المحلول من 5.0 الى 5.1 pH وبزيادة كثافة التيار المستخدم للترسيب من 100 الى 400 nm. تم كبس الدقائق النانوية النحاسية المنتجة لإنتاج قرص يستخدم كمرشح للغازات تم تحديد النفاذية والمسامية وكفاءة الترشيح، والتي اظهرت كفاءة جيدة للمرشح.

Introduction

Metal nanoparticles have attracted much attention in nanoscale science and engineering technology over the past decade due to their unusual chemical and physical properties, such as catalytic activity, and novel electronic, optical and magnetic properties [1]. Their main application areas

include catalysts, absorbents, chemical and biological sensors, optoelectronics, information storage, and photonic and electronic devices [2]. Various methods, such as wet chemical reduction, reverse micelles, and electrochemical and sonoelectrochemical deposition techniques [3]. Copper nanoparticles have been considered by many researchers in the past two decades due to special features including optical, electrical properties [4]. Among of methods used to synthesize copper nanoparticles, we can refer to sonoelectrodeposition method.

Sonoelectrochemistry is the coupling of ultrasonic vibration to an electrochemical system [5]. Recently there is a growing interest of the application of the sonoelectrodeposition in the preparation of nanopowders [6]. Sonoelectrodeposition method is a simple environmental friendly and cost effectiveness method used to produce metallic nanosized materials compared to most of other methods including radiation, thermal decomposition, and vapor deposition, reduction in microemulsions and chemical reduction [7].

Experimental

Materials and method

Sonoelectrodeposition technique was used to prepare CuNPs at different solution acidity (pH=0.5, 1 and 1.5) and different current density (100, 200, 300 and 400 mA/cm^2) at 20 ^oC. The setup consists of titanium horn with (20 kHz) acts both as a cathode and an ultrasound emitter, and copper sheet as anode. The immersed part of the Ti probe, about 2 cm into the electrolyte, is covered by an isolating plastic except the circular surface electro-active part. The probe is connected to a pulsed power supply. The electrolyte bath was prepared by dissolving 0.5g of copper sulfate in 250 mL distilled water. The pH was adjusted, using pH-meter, by adding some drops of H_2SO_4 acid to the solution. The power supply was activated. After 1 minute, the electrolyte would gradually start to turn an opaque red. This color indicated that large quantities of copper particles were in suspension. The powder was collected using a centrifugation technique and dried at room temperature.

Characterization

The prepared CuNPs were examined by X-ray diffraction and SEM to study the structure and NPs size at different conditions. Finally copper nanoparticles with nano size were used to make a disk filter by pressing 5 g of copper powders in piston with 15 mm diameter to produce of 3 mm disc thickness. This disc is placed in a special sealed holder. Fig.1 shows the hand-made device used to evaluate the CuNPs filter.

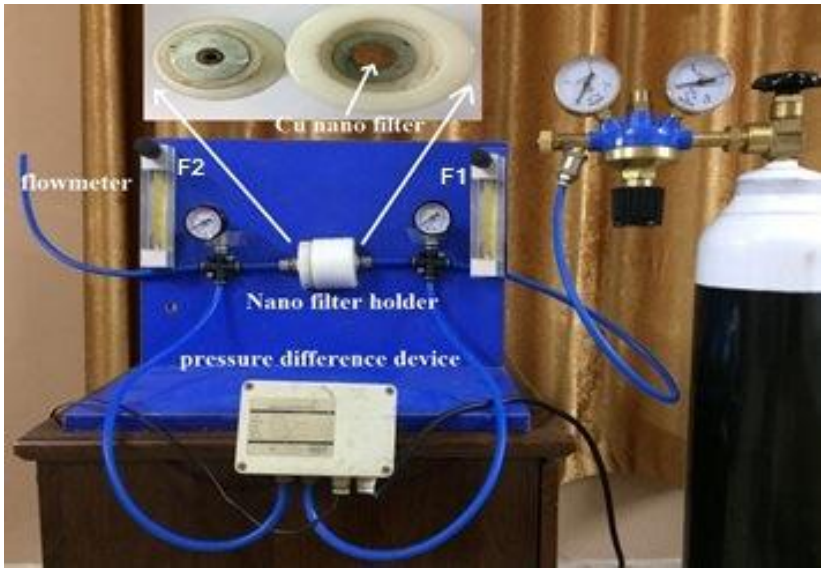

Fig. 1: Gas filter evaluation system.

The system consists two Teflon pieces; the filter is placed between them and tightly sealed. It has two sides for the entry and exit of the tested gas and is connected to a device to measure the pressure difference between the two sides and gas flow measurement.

Results and discussion

The crystallinety of the produced CuNPs at all pH values were examined by XRD, as shown in Fig. 2, these spectra revealed a nanosized crystallites partially oxidized copper nanoparticles at all (0.5, 1 and 1.5) pH values using 100 mA/cm^2 current density.

The order of the variation of the crystallite size are somehow different from the results estimated using SEM techniques, this may attributed to the fact that the crystallite size deduced using Scherrer equation is totally different from particle size or grain size, so this results will not useful to confirm the effect of acidity on the particle size.

The analysis of the main Cu peak at 2θ of 43.75^{o} was shown in Fig. 3, the FWHM (and the crystallite size) of pH 0.5, 1.0 and 1.5 are 0.103^{o} (45 nm), 153^{o} (38 nm) and 0.172^{o} (37 nm) respectively. All XRD data are listed in Table 1.

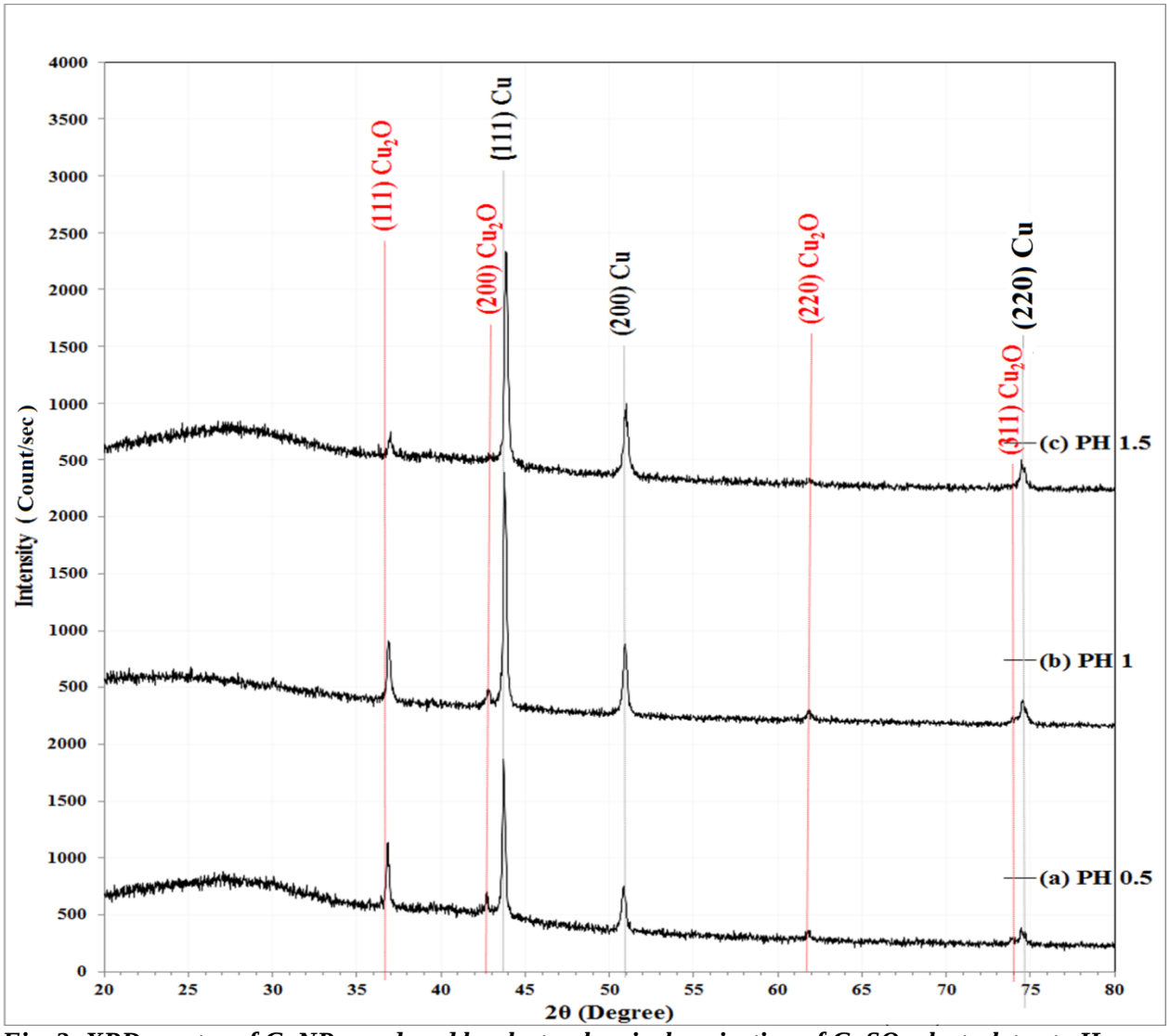

Fig. 2: XRD spectra of CuNPs produced by electrochemical sonication of $CuSO_4$ electrolyte at pH a) 0.5, b)1.0 and c)1.5 for 1min with sonication power of 400 W.

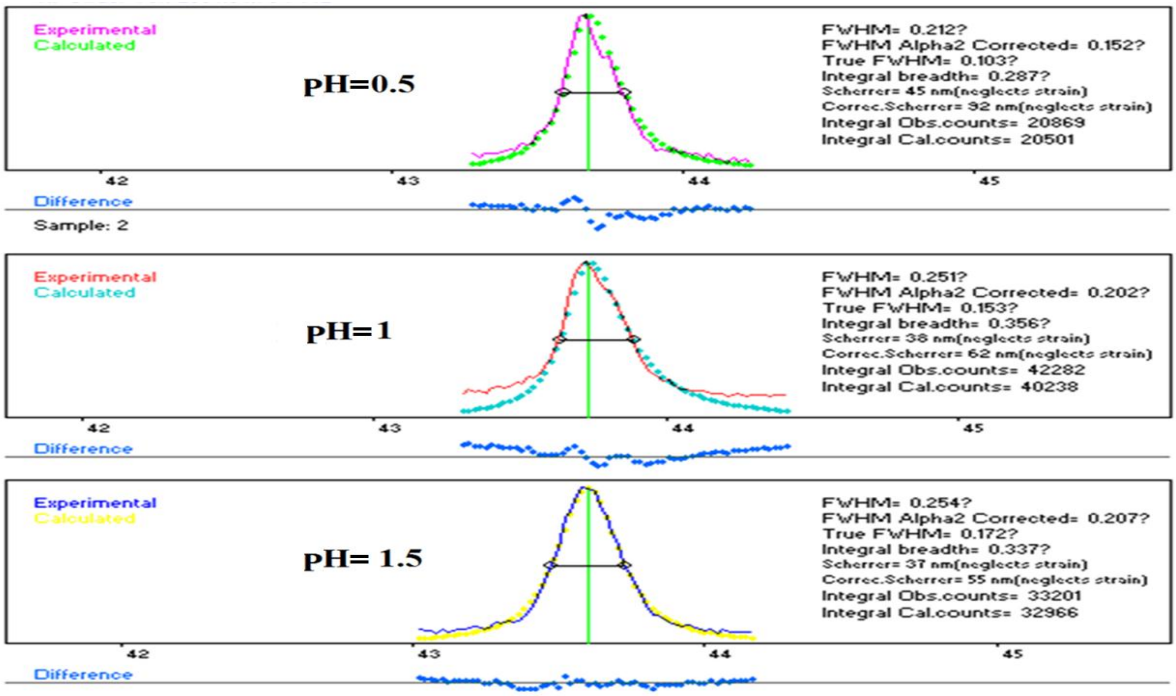

Fig. 3: XRD preferred peak profile for Cu along (111) direction at different pH (0.5, 1 and 1.5).

Table 1: XRD data of CuNPs produced by electrochemical sonication of $CuSO_4$ electrolyte at different pH (0.5, 1 and 1.5), for 1min with sonication power of 400 W.

pH	2θ (Deg.)	FWHM (Deg.)	d_{hkl} Exp.(Å)	G.S (nm)	d_{hkl} Std.(Å)	hkl	Phase
0.5	36.8447	0.2058	2.4375	40.7	2.4644	(111)	Cu_2O
	42.6948	0.2057	2.1161	41.5	2.1342	(200)	Cu_2O
	43.7237	0.212	2.0686	40.4	2.1316	(111)	Cu
	50.8378	0.3822	1.7946	23.0	1.8460	(200)	Cu
	61.803	0.3822	1.4999	24.2	1.5091	(220)	Cu_2O
	73.856	0.294	1.2821	33.8	1.2870	(311)	Cu_2O
	74.4439	0.3822	1.2734	26.1	1.3053	(220)	Cu
1	36.8741	0.294	2.4356	28.5	2.4644	(111)	Cu_2O
	42.7536	0.294	2.1133	29.0	2.1342	(200)	Cu_2O
	43.7825	0.251	2.0660	34.1	2.1316	(111)	Cu
	50.926	0.3234	1.7917	27.2	1.8460	(200)	Cu
	61.8618	0.4409	1.4986	21.0	1.5091	(220)	Cu_2O
	74.5321	0.3822	1.2721	26.1	1.3053	(220)	Cu
1.5	36.9917	0.2646	2.4282	31.7	2.4644	(111)	Cu_2O
	43.8413	0.254	2.0634	33.7	2.1316	(111)	Cu
	50.9848	0.3234	1.7898	27.2	1.8460	(200)	Cu
	74.4733	0.3528	1.2730	28.3	1.3053	(220)	Cu

Fig. 4 shows the SEM images of CuNPs produced at different acidic $CuSO_4$ (pH=0.5, 1 and 1.5) and different current densities (100, 200, 300 and 400 mA). These images reflect clearly that the particle size have increased with increasing current density, the average particles size which estimated using ImageJ program were; 22, 37, 42 and 68 nm using 100, 200, 300, and 400 mA/cm^2 respectively at 0.5 pH, some published papers reported same manners and the others not agreed with this trends [8-10]. At (pH=1.0) the average particles size values showed similar behavior with the applied current density. The particle size increased with increasing current density, but with less

differences, they were; 31, 38, 44, 69 nm using 100, 200, 300, and 400 mA/cm^2 respectively, while the average diameters of the CuNPs produced in pH of 1.5 at different current densities have a few variation (72, 74, 76 and 77nm).

Table 2 summarizes the results of the produced CuNPs at different pH and different current density with the required deposition potential. These data reflected a fact that increasing current density at less acidic copper sulfate have little effect on the particle size of the produced CuNPs and it is higher than the particle size produces at the higher acidic electrolyte [11].

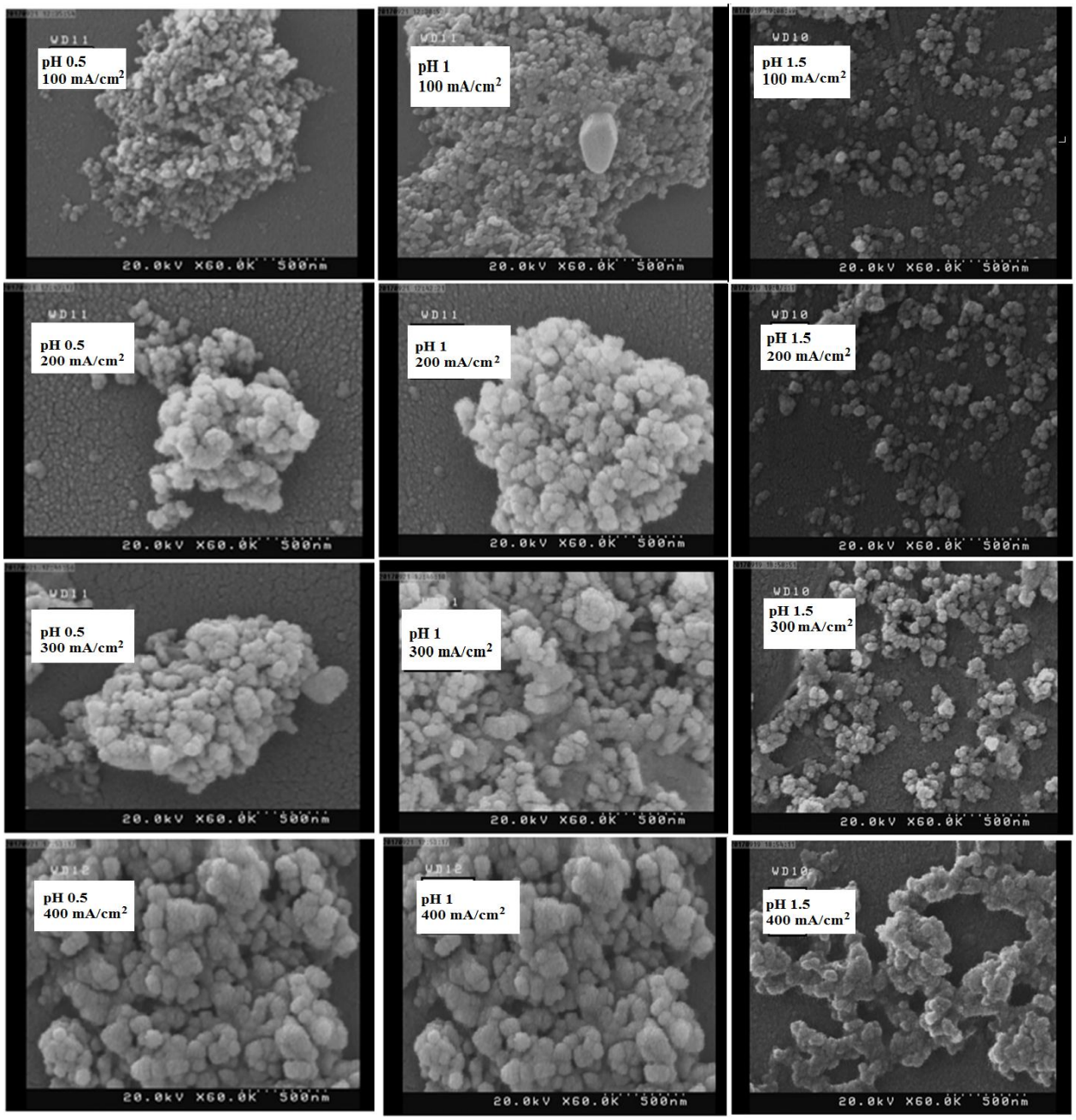

Fig. 4: SEM images of Cu NPs produced by electrochemical sonication of $CuSO_4$ electrolyte at pH 0.5, 1 and 1.5 and different current density of 100, 200, 300, and 400 mA/cm^2, for 1min with sonication power of 400W sonication.

Table 2: Average particle size of the produced CuNPs from $CuSO_4$ solution at different pH and different current density with the required deposition potential.

pH	Current density (mA/cm^2)	Deposition Voltage (V)	Average particle size (nm)
0.5	**100**	2.10	22
	200	3.23	37
	300	4.63	42
	400	4.98	68
1	**100**	2.4	31
	200	4.11	38
	300	5.02	44
	400	6.21	69
1.5	**100**	4.30	72
	200	6.17	74
	300	8.32	76
	400	10.01	77

The porosity of fabricated CuNPs filter disks decrease with increasing average particle diameters [12] so there are a different in filter permeability. The permeability was measured and calculated using Darcy's law:

$$F = A\ P\ \Delta p / V\ D \quad (1)$$

where: F is the flow rate ($cm^3.min^{-1}$), A is the area of filter (cm^2), P is the permeability (m^2), Δp(barr) is the pressure differences between the inlet and the outlet of the Teflon containers, V is the air or N_2 viscosity ($18.27*10^{-6}$ Pa.s), D is the thickness of CuNPs filter (μm).

The two flow meters were are used to measure the inlet and outlet gas flow which used then to measure the filtration efficiency;

$$FE\ \% = [\ (F_{inlet} - F_{outlet}) / F_{inlet}\ ] \times 100 \quad (2)$$

where FE is the filtration efficiency, F_{inlet}, F_{outlet} are the measured inlet and outlet gas flow rates. 1 and 2, taking disk area as 1.5×10^{-4} m^2, disk thickness as 3×10^{-3} m, and N_2 gas kinematic viscosity as ($1.647*10^{-5}$ $N.s/m^2$) [13], all results were listed in Table 3.

Table 3: Porosity, permeability and filtration efficiency of CuNPs filter disk.

Filter with Average Particle size	CuNPs Preparation conditions (pH, mA/cm^2)	Porosity% Image j	Permeability(P)			F_{in}	F_{out}	FE %
			$F\times10^{-6}$ (m^3/s)	ΔP (Pa)	$K_P\times 10^{-14}$ (m^2)			
$1_{(26nm)}$	0.5, 100	48	1.467	3900	12.38	88	17	80.6
$2_{(35nm)}$	1.0, 200	36	1.467	4210	11.47	88	27	69.3
$3_{(69nm)}$	1.5, 400	24	1.467	5200	9.29	88	33	62.5
$1_{(26nm)} + 2_{(35nm)} + 3_{(69nm)}$		42	1.467	4020	12.01	88	19	78.4

The filter porosity is a static parameter which gives information about the initial state of the filter disk. The porosity is highly depends on CuNPs diameter and it reduced with increasing the particles diameters, which is mainly due to high free surface area to the volume [13]. From mechanical view, the smaller particle diameter narrow range of CuNPs filter disks seems to be weak and sometimes it is destructed on pressing it inside the Teflon filter housing. On the other hand using mixed varied particle diameter led to enhanced cohesion and porosity, porosity adequate enough to avoid the pressure drop [14].

Conclusions

The sonoelectrodeposition technique is an effective way to produce large quantities of copper nanoparticles in short time. The variation of solution acidity and used current density is an effective way to control the size of produced copper nanoparticles.

In general, increasing current density and pH cause to increase NPs diameters but at less acidic (1.5 pH) the current have little effect on the particle size of the produced CuNPs and it is higher than the particle size produces at the higher acidic electrolyte.

Nano filter with good efficiency and high quality was prepared by using CuNPs with different diameters.

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